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Negoro et al.

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(54) **SUBSTRATE PROCESSING METHOD AND SUBSTRATE PROCESSING APPARATUS**

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(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **14/475,069**

(22) Filed: **Sep. 2, 2014**

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(30) **Foreign Application Priority Data**

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Sep. 2, 2013 (JP) 2013-181510

(51) **Int. Cl.**

B44C 1/22	(2006.01)
C23F 1/00	(2006.01)
C03C 15/00	(2006.01)
C03C 25/68	(2006.01)
H01L 21/302	(2006.01)
H01L 21/461	(2006.01)
C11D 11/00	(2006.01)
H01L 21/67	(2006.01)
C11D 3/00	(2006.01)

(52) **U.S. Cl.**

CPC *C11D 11/0047* (2013.01); *C11D 3/0052* (2013.01); *C11D 11/007* (2013.01); *C11D 11/0064* (2013.01); *H01L 21/67028* (2013.01); *H01L 21/67051* (2013.01)

(58) **Field of Classification Search**

USPC 216/83
See application file for complete search history.

(56) **References Cited**

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Primary Examiner — Thomas Pham
(74) *Attorney, Agent, or Firm* — Ostrolenk Faber LLP

(57) **ABSTRACT**

A substrate processing method includes an SPM supplying step of supplying SPM having high temperature to an upper surface of a substrate, a DIW supplying step of supplying, after the SPM supplying step, DIW having room temperature to the upper surface of the substrate to rinse off a liquid remaining on the substrate, and a hydrogen peroxide water supplying step of supplying, after the SPM supplying step and before the DIW supplying step, hydrogen peroxide water of a liquid temperature lower than the temperature of the SPM and not less than room temperature, to the upper surface of the substrate in a state where the SPM remains on the substrate.

6 Claims, 20 Drawing Sheets

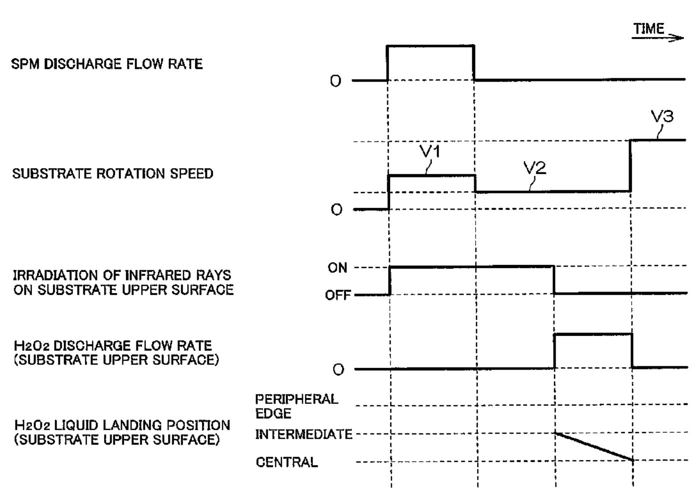


FIG. 1

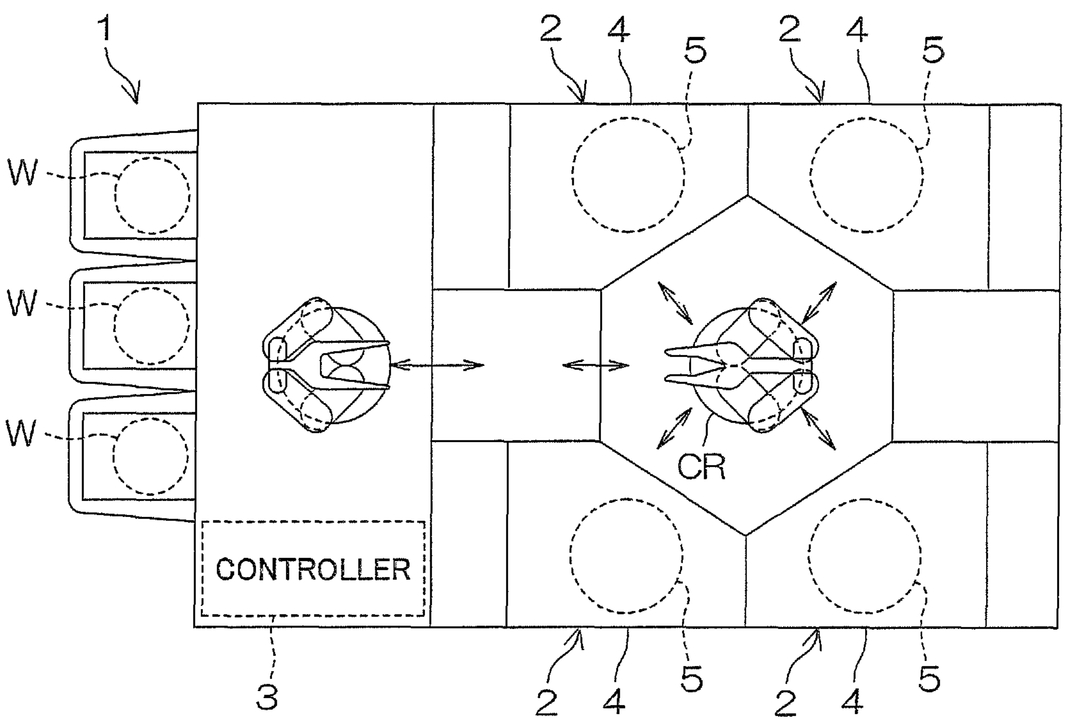
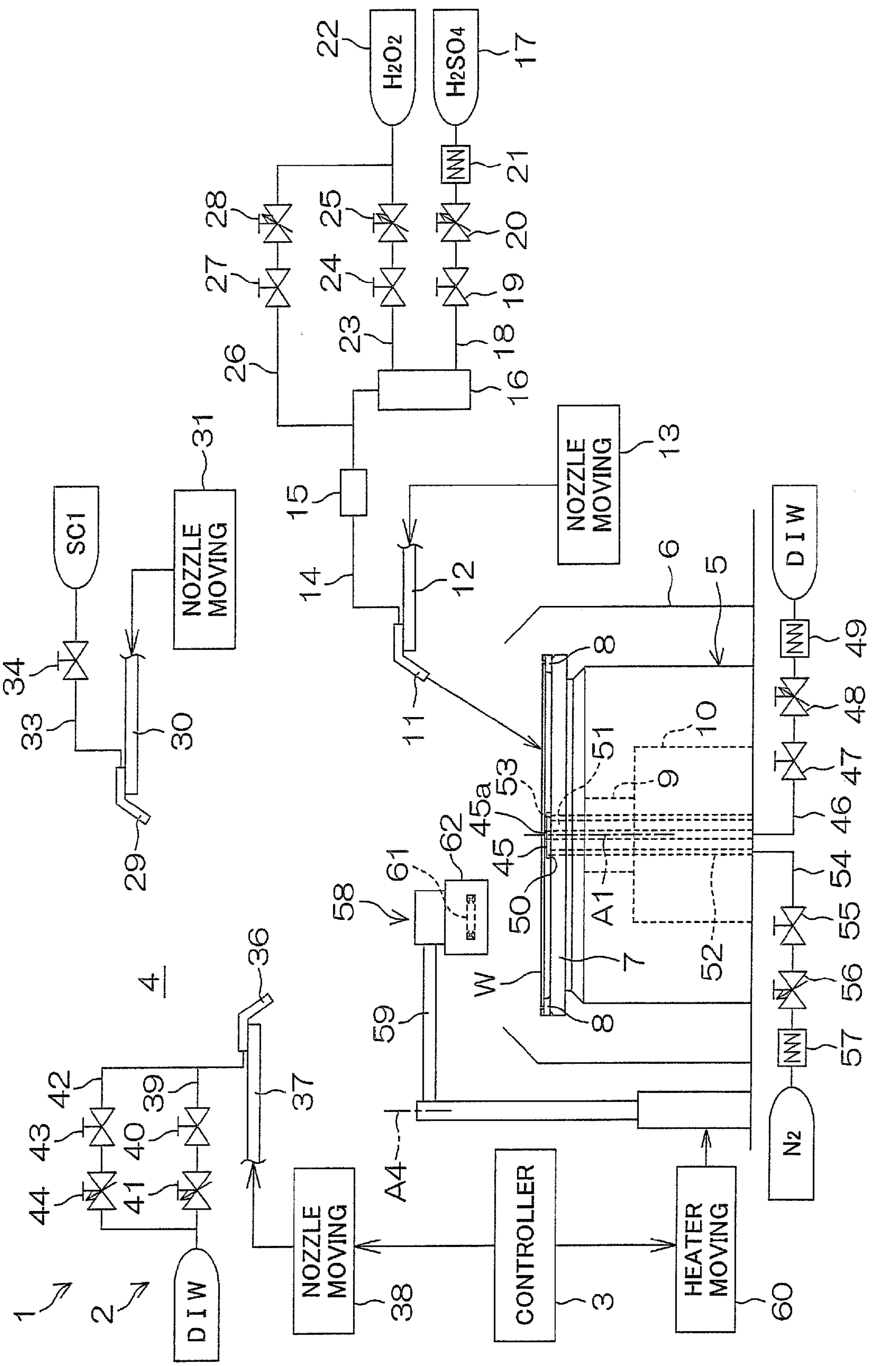


FIG. 2



H2O2
H2SO4
SC1
NOZZLE MOVING
NOZZLE MOVING
NOZZLE MOVING
CONTROLLER
HEATER MOVING
D I W
D I W
N2
W
A1
A4

FIG. 3

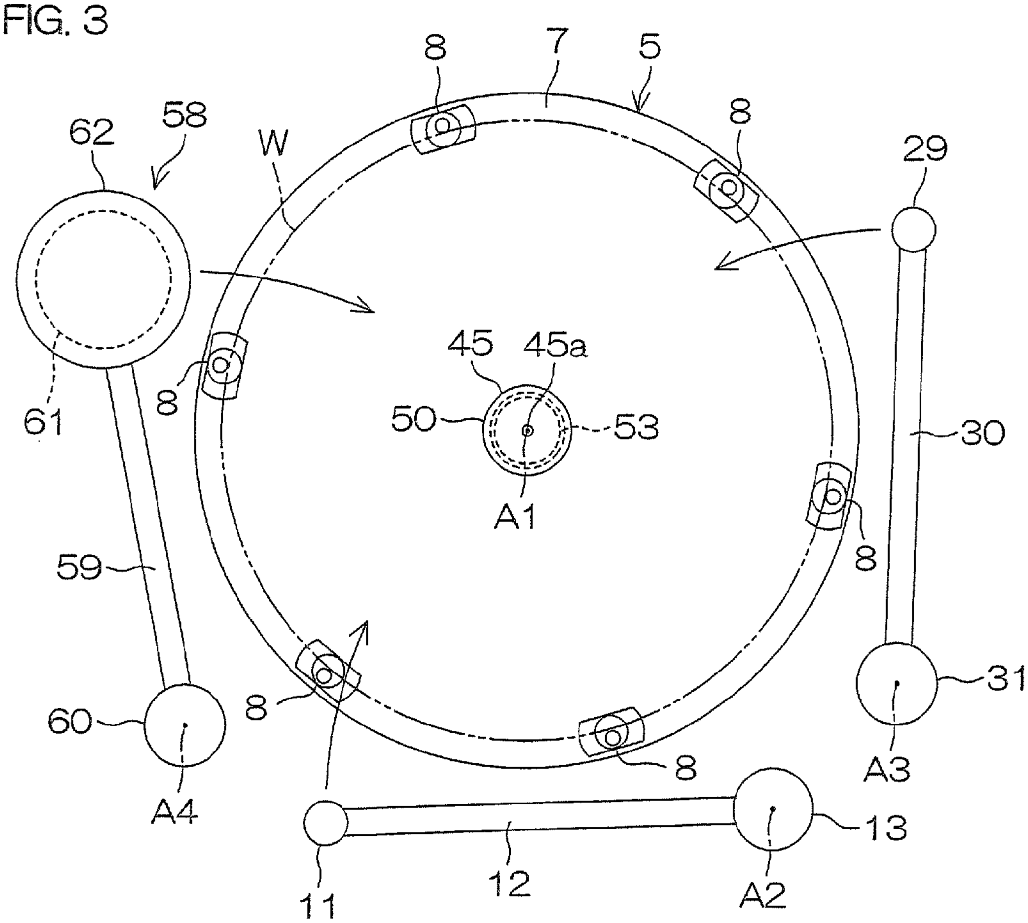

8
7
5
8
62
58
W
29
45
45a
50
53
61
8
30
A1
8
59
31
60
8
8
A3
A4
13
11
12
A2

FIG. 4

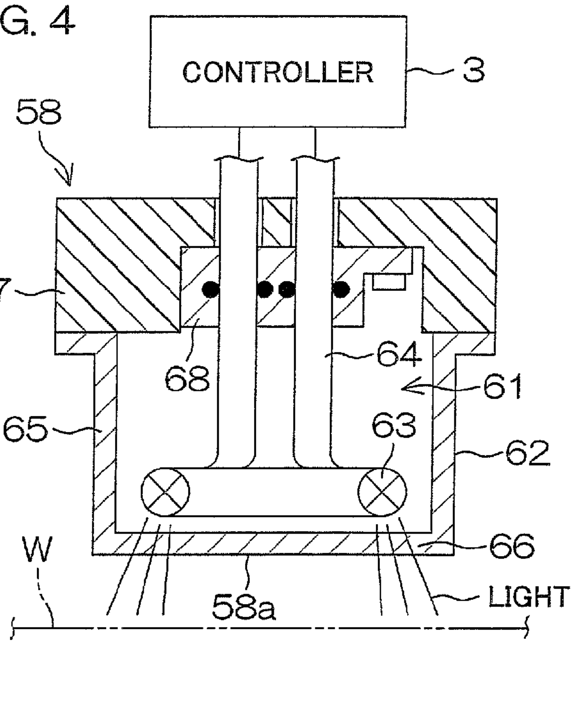

CONTROLLER
3
58
67
68
64
61
65
63
62
66
W
58a
LIGHT

FIG. 5

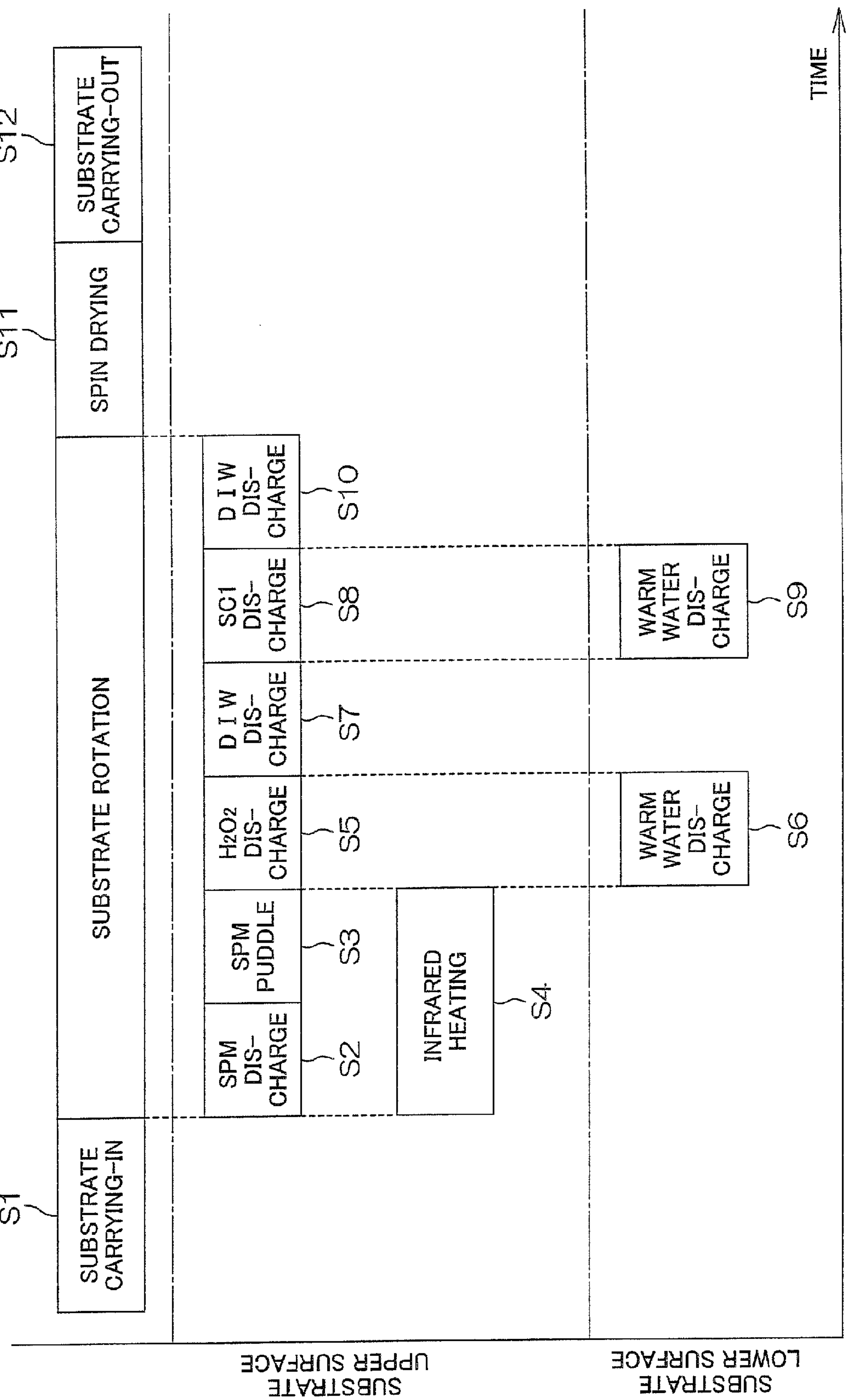

SUBSTRATE UPPER SURFACE
SUBSTRATE LOWER SURFACE
TIME
S1
SUBSTRATE CARRYING-IN
SUBSTRATE ROTATION
S2
SPM DIS-CHARGE
S3
SPM PUDDLE
S4
INFRARED HEATING
S5
H_2O_2 DIS-CHARGE
S6
WARM WATER DIS-CHARGE
S7
D I W DIS-CHARGE
S8
SC1 DIS-CHARGE
S9
WARM WATER DIS-CHARGE
S10
D I W DIS-CHARGE
S11
SPIN DRYING
S12
SUBSTRATE CARRYING-OUT

FIG. 6A

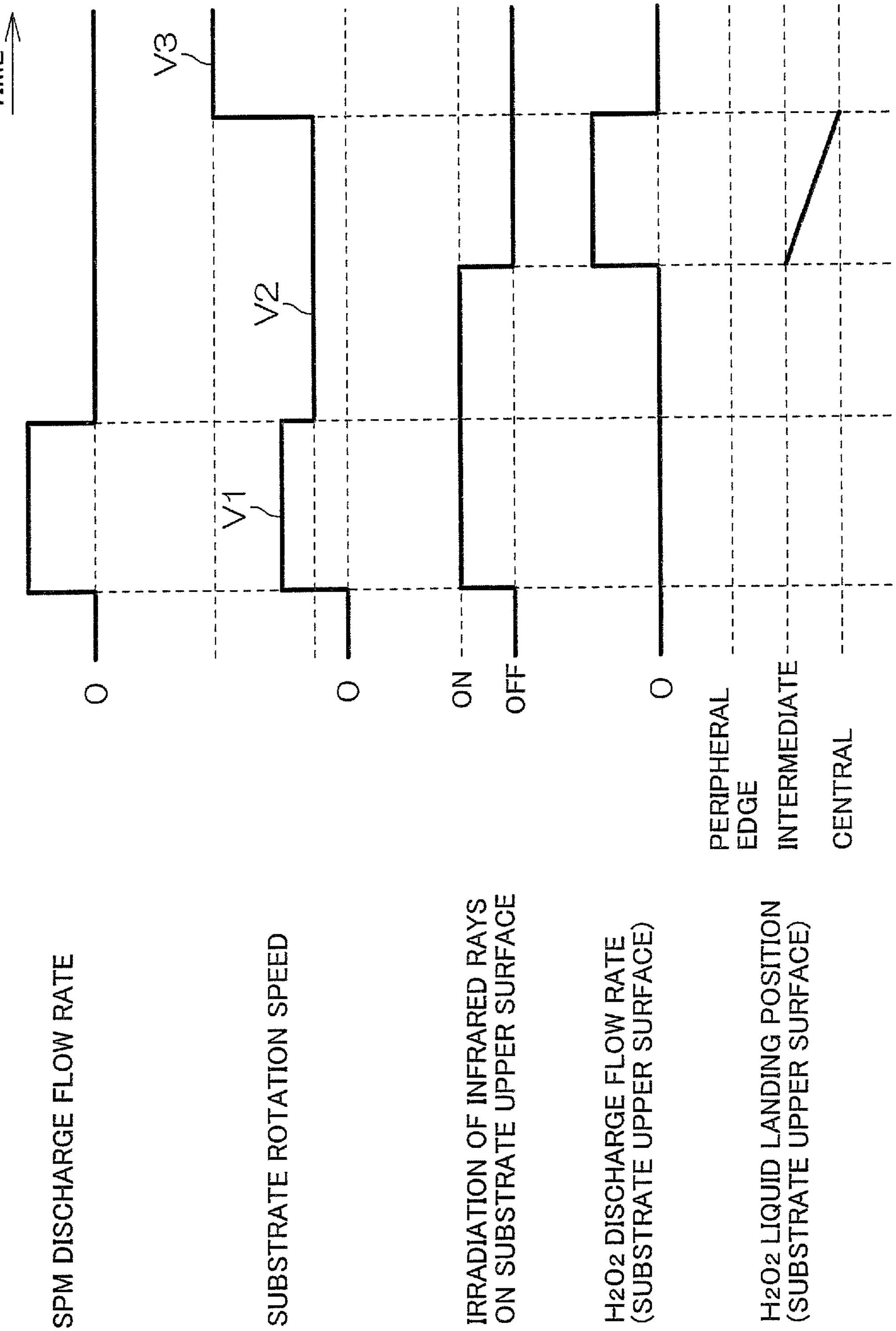

TIME
SPM DISCHARGE FLOW RATE
0
SUBSTRATE ROTATION SPEED
V1
V2
V3
0
IRRADIATION OF INFRARED RAYS ON SUBSTRATE UPPER SURFACE
ON
OFF
H_2O_2 DISCHARGE FLOW RATE (SUBSTRATE UPPER SURFACE)
0
H_2O_2 LIQUID LANDING POSITION (SUBSTRATE UPPER SURFACE)
PERIPHERAL EDGE
INTERMEDIATE
CENTRAL

FIG. 6B

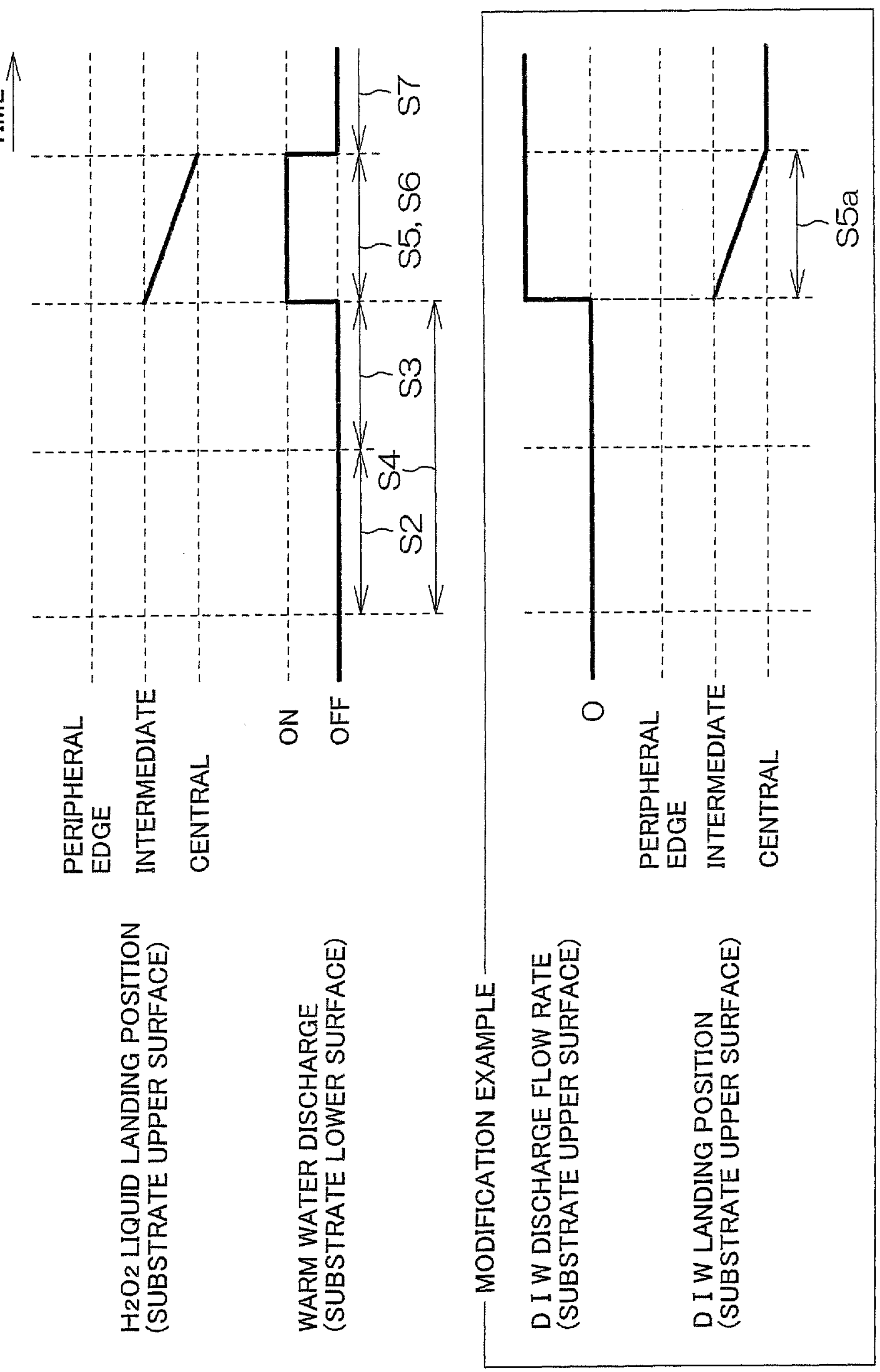

TIME
H_2O_2 LIQUID LANDING POSITION
(SUBSTRATE UPPER SURFACE)
PERIPHERAL EDGE
INTERMEDIATE
CENTRAL
WARM WATER DISCHARGE
(SUBSTRATE LOWER SURFACE)
ON
OFF
S2
S4
S3
S5, S6
S7
MODIFICATION EXAMPLE
D I W DISCHARGE FLOW RATE
(SUBSTRATE UPPER SURFACE)
0
D I W LANDING POSITION
(SUBSTRATE UPPER SURFACE)
PERIPHERAL EDGE
INTERMEDIATE
CENTRAL
S5a

FIG. 7A

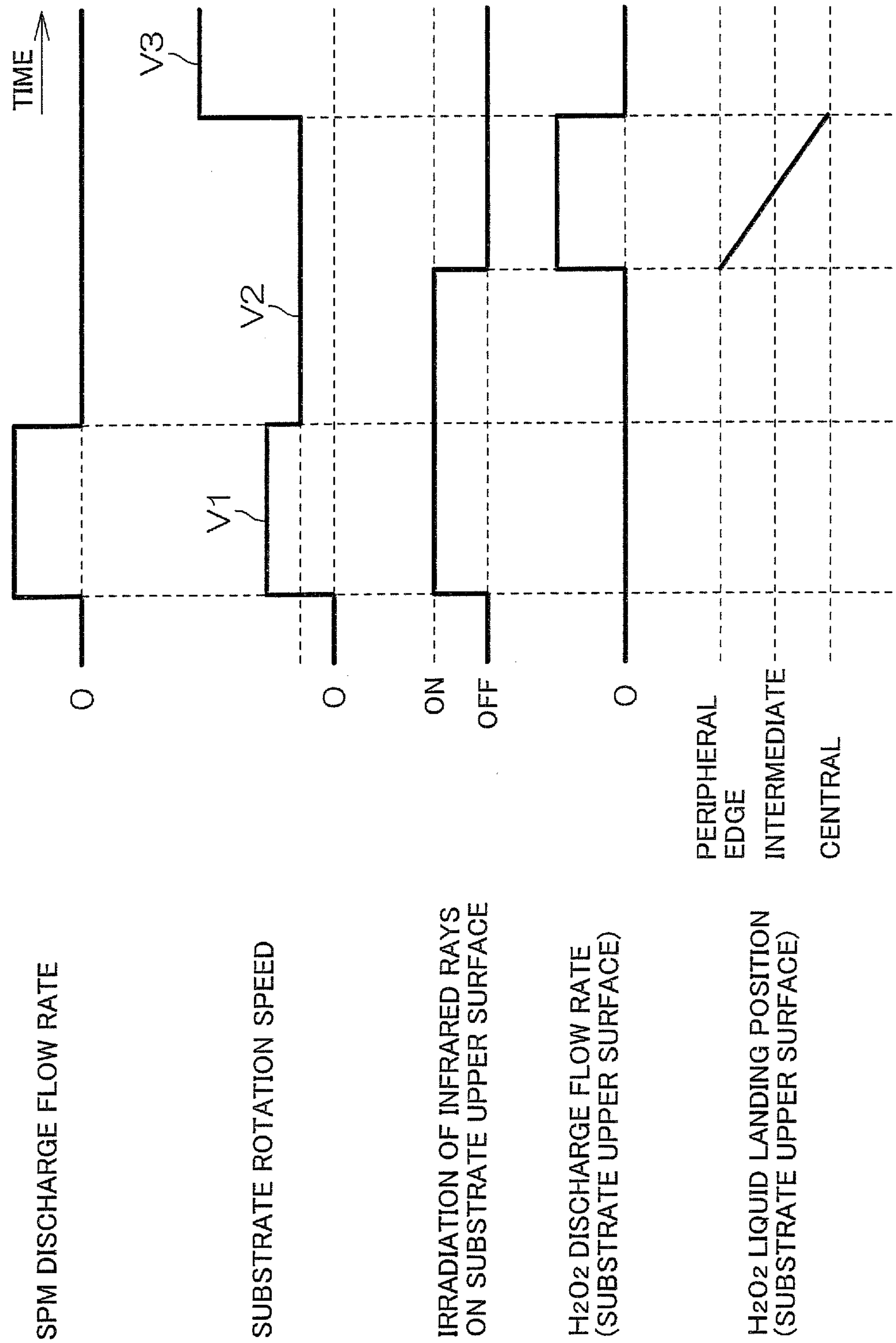

SPM DISCHARGE FLOW RATE
SUBSTRATE ROTATION SPEED
IRRADIATION OF INFRARED RAYS ON SUBSTRATE UPPER SURFACE
H_2O_2 DISCHARGE FLOW RATE (SUBSTRATE UPPER SURFACE)
H_2O_2 LIQUID LANDING POSITION (SUBSTRATE UPPER SURFACE)
0
0
ON
OFF
0
PERIPHERAL EDGE
INTERMEDIATE
CENTRAL
TIME
V1
V2
V3

FIG. 7B

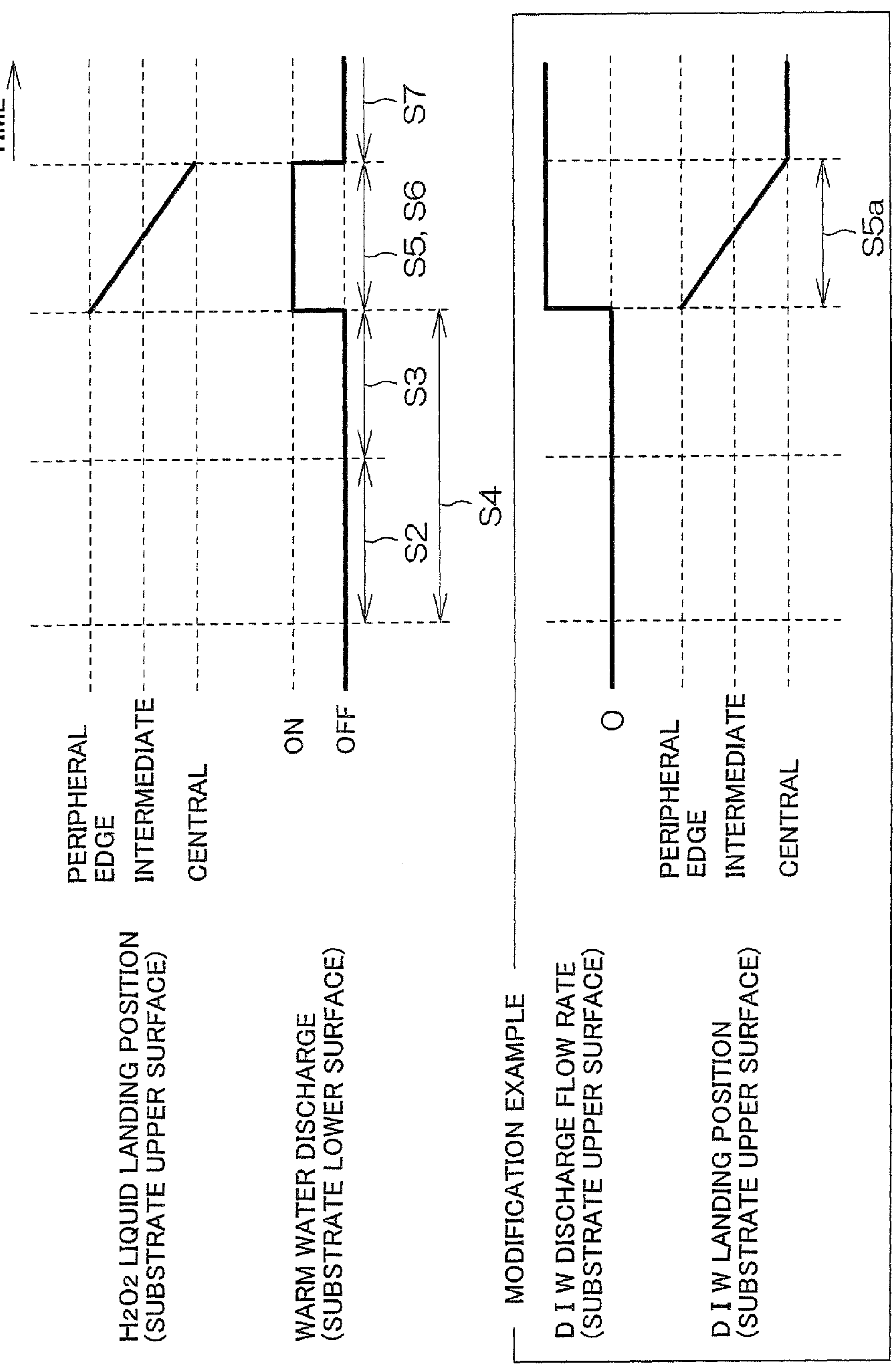

TIME
H2O2 LIQUID LANDING POSITION
(SUBSTRATE UPPER SURFACE)
PERIPHERAL EDGE
INTERMEDIATE
CENTRAL
WARM WATER DISCHARGE
(SUBSTRATE LOWER SURFACE)
ON
OFF
S2
S3
S4
S5, S6
S7
MODIFICATION EXAMPLE
D I W DISCHARGE FLOW RATE
(SUBSTRATE UPPER SURFACE)
0
D I W LANDING POSITION
(SUBSTRATE UPPER SURFACE)
PERIPHERAL EDGE
INTERMEDIATE
CENTRAL
S5a

FIG. 8

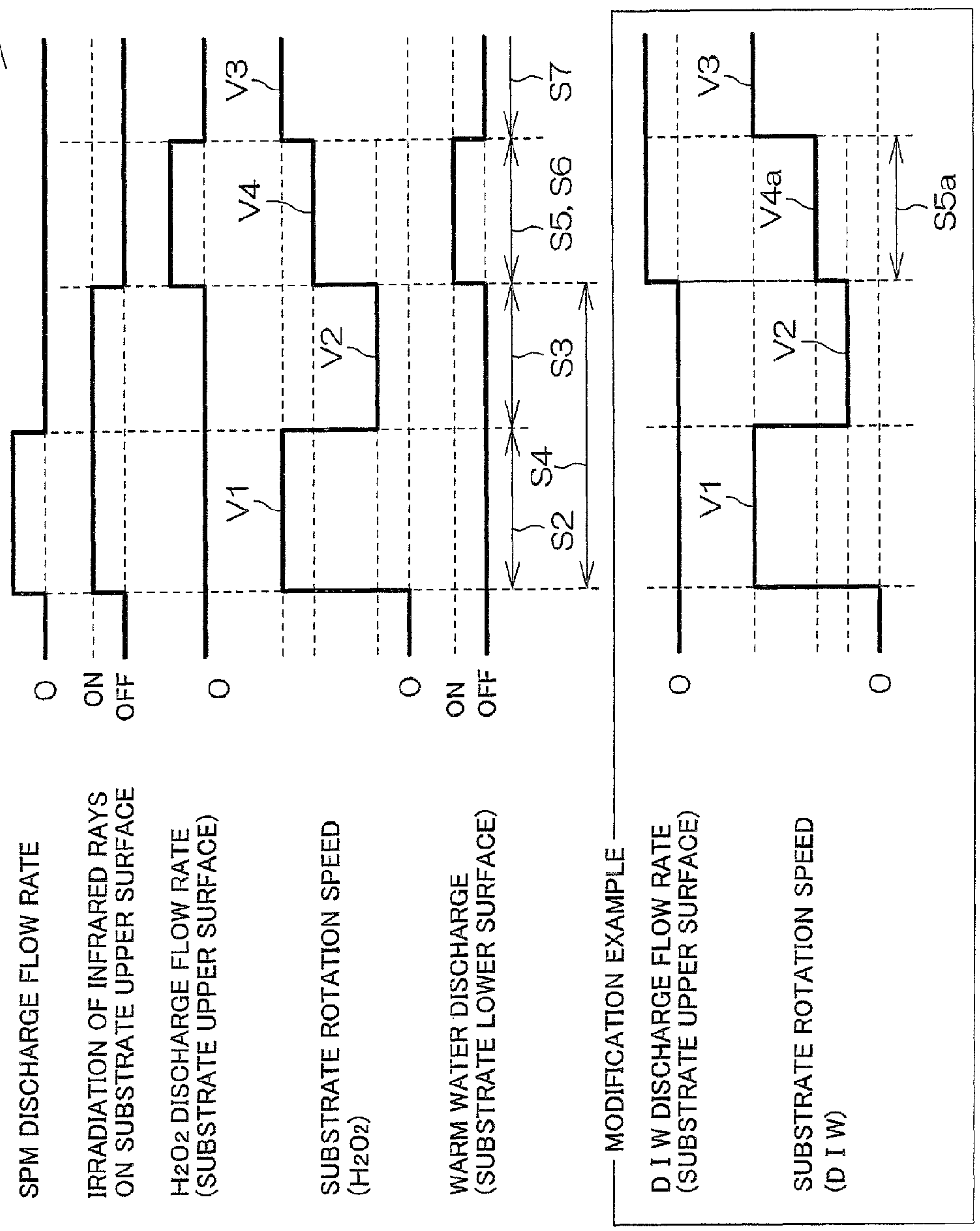

TIME
SPM DISCHARGE FLOW RATE
IRRADIATION OF INFRARED RAYS ON SUBSTRATE UPPER SURFACE
H2O2 DISCHARGE FLOW RATE (SUBSTRATE UPPER SURFACE)
SUBSTRATE ROTATION SPEED (H2O2)
WARM WATER DISCHARGE (SUBSTRATE LOWER SURFACE)
MODIFICATION EXAMPLE
D I W DISCHARGE FLOW RATE (SUBSTRATE UPPER SURFACE)
SUBSTRATE ROTATION SPEED (D I W)
0
ON
OFF
V1
V2
V3
V4
V4a
S2
S3
S4
S5, S6
S5a
S7

FIG. 9

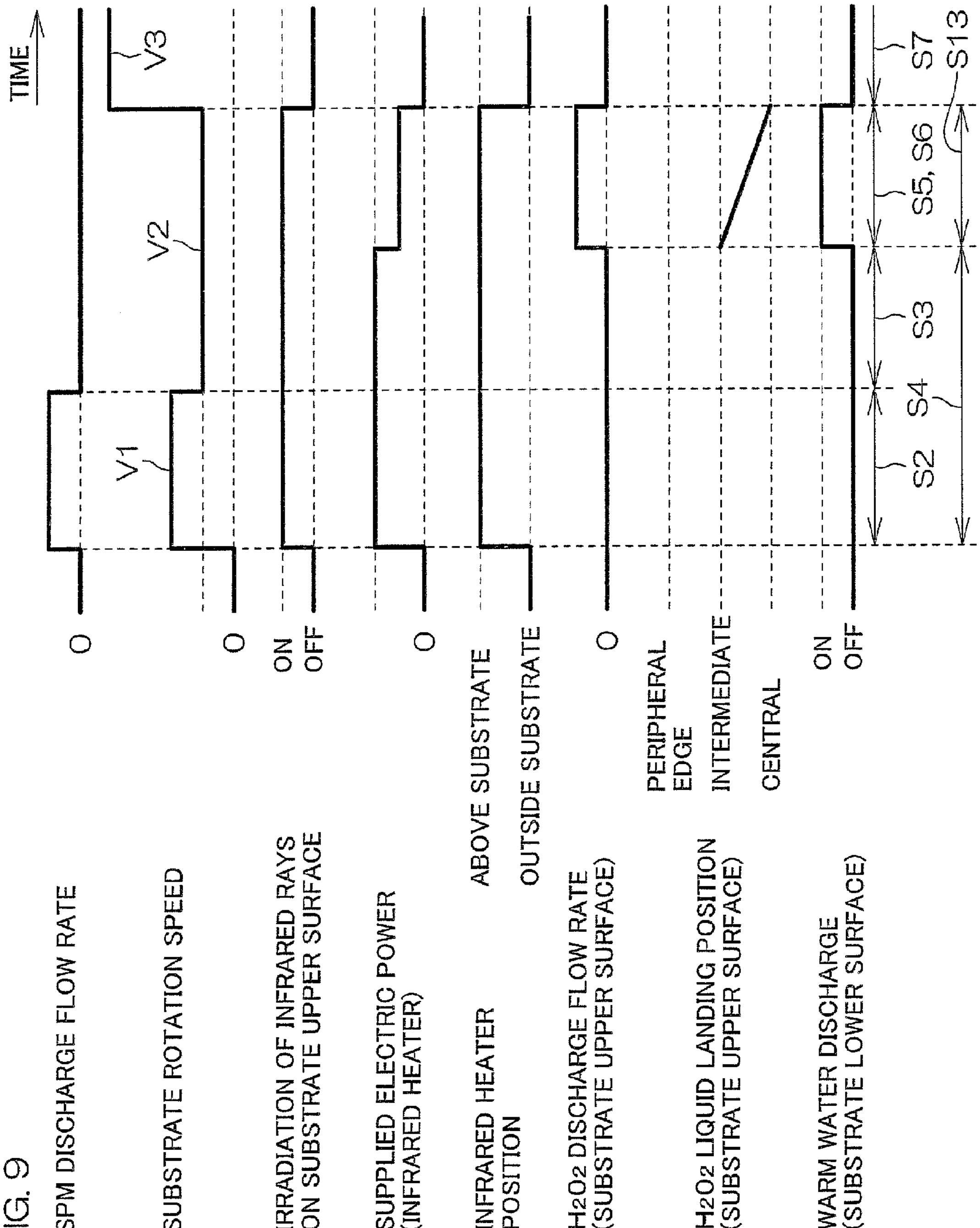

TIME
SPM DISCHARGE FLOW RATE
0
SUBSTRATE ROTATION SPEED
0
V1
V2
V3
IRRADIATION OF INFRARED RAYS ON SUBSTRATE UPPER SURFACE
ON
OFF
SUPPLIED ELECTRIC POWER (INFRARED HEATER)
0
INFRARED HEATER POSITION
ABOVE SUBSTRATE
OUTSIDE SUBSTRATE
H_2O_2 DISCHARGE FLOW RATE (SUBSTRATE UPPER SURFACE)
0
H_2O_2 LIQUID LANDING POSITION (SUBSTRATE UPPER SURFACE)
PERIPHERAL EDGE
INTERMEDIATE
CENTRAL
WARM WATER DISCHARGE (SUBSTRATE LOWER SURFACE)
ON
OFF
S2
S4
S3
S5, S6
S7
S13

FIG. 10

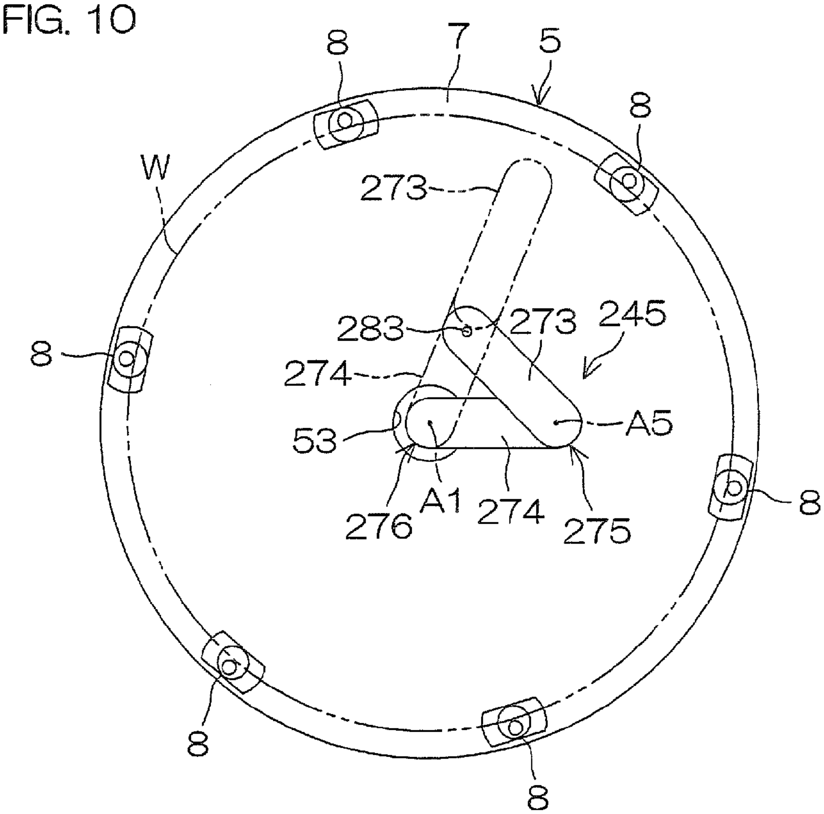

8
7
5
8
W
273
283
273
245
8
274
53
A5
A1
274
276
275
8
8
8

FIG. 11

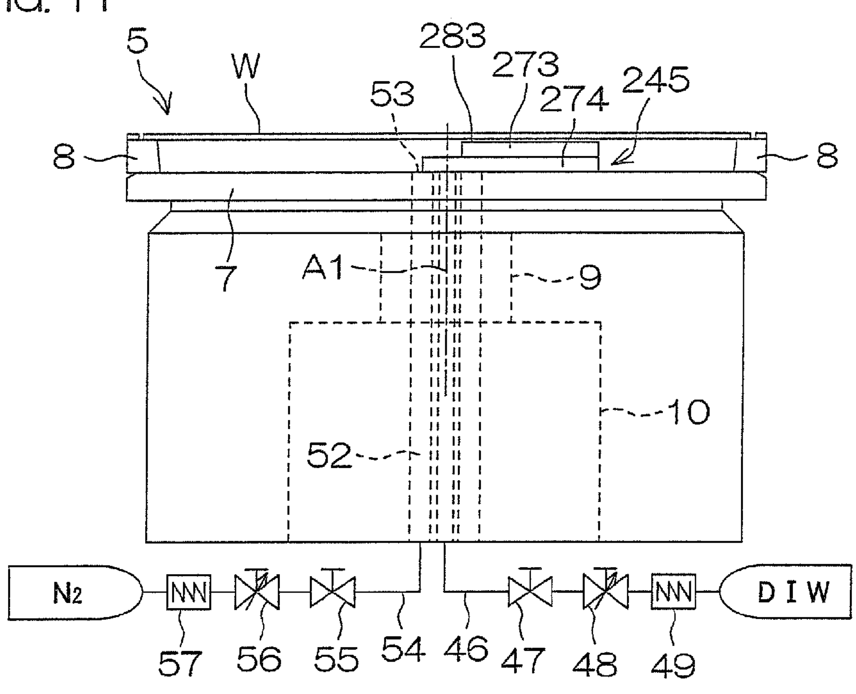

5
W
283
273
53
274
245
8
8
7
A1
9
10
52
N2
DIW
57
56
55
54
46
47
48
49

FIG. 12

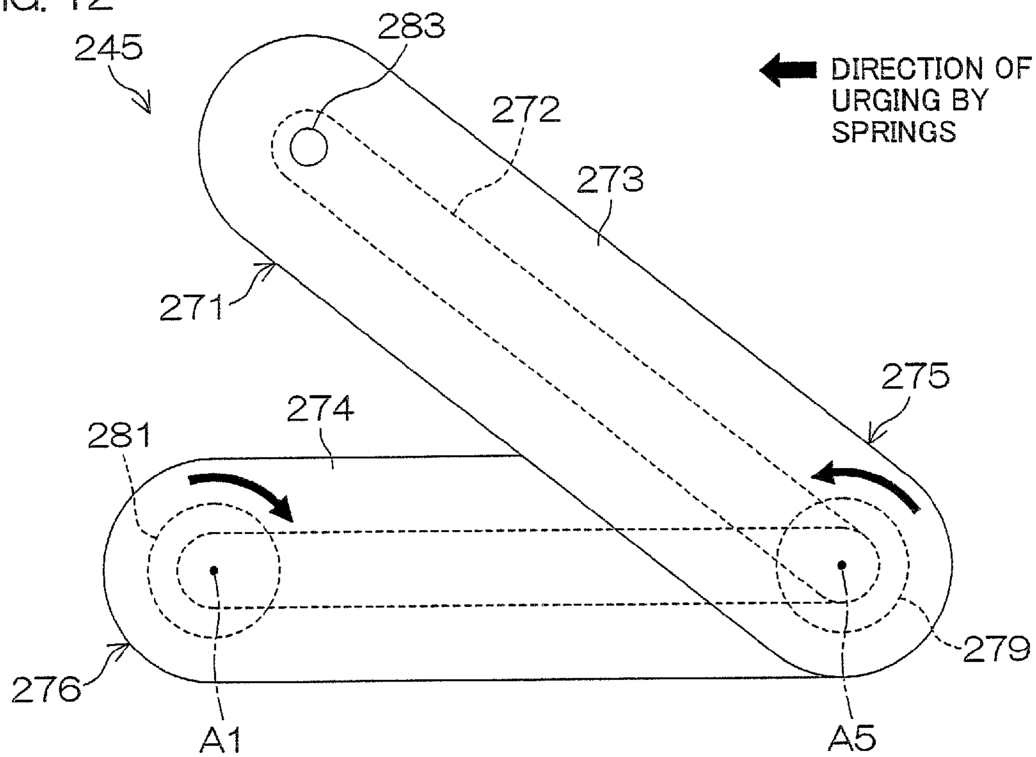

245
283
272
273
DIRECTION OF
URGING BY
SPRINGS
271
275
274
281
279
276
A1
A5

FIG. 13

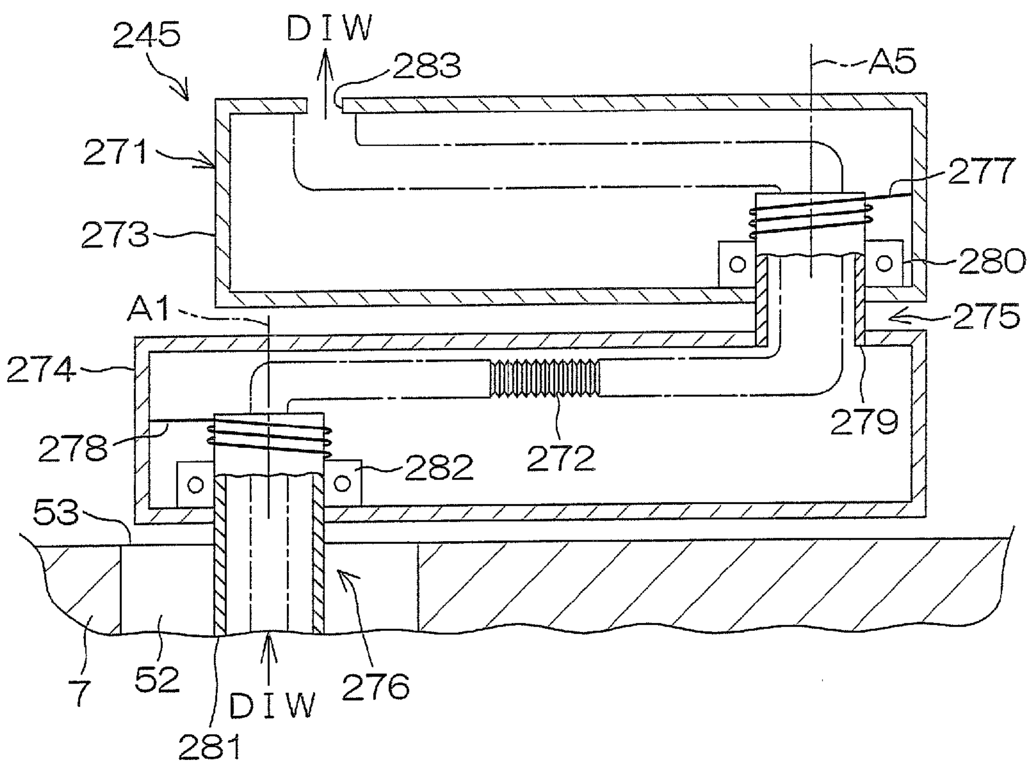

245
DIW
283
A5
271
277
273
280
A1
275
274
278
282
272
279
53
7
52
281
DIW
276

FIG. 14

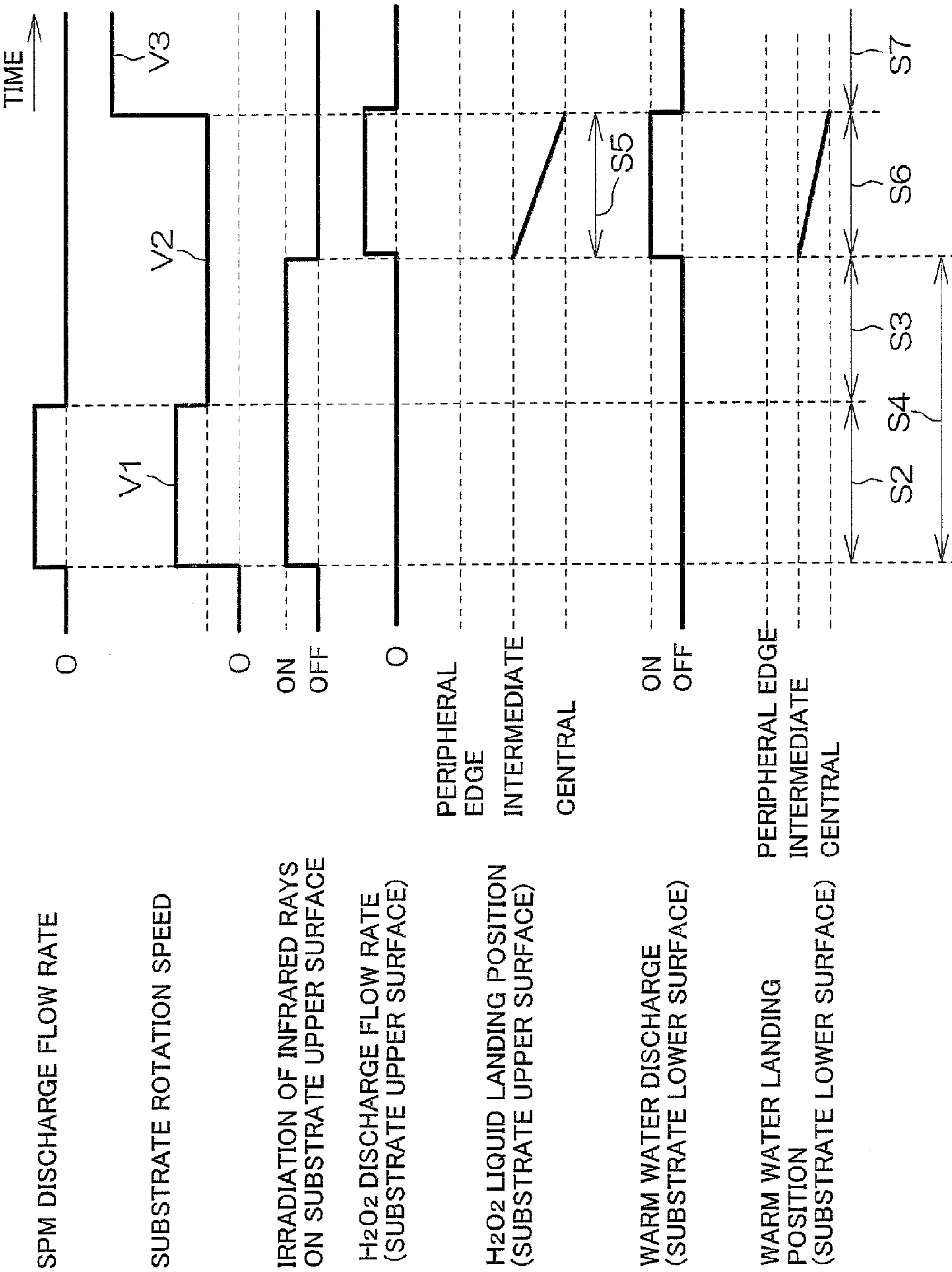

SPM DISCHARGE FLOW RATE
SUBSTRATE ROTATION SPEED
IRRADIATION OF INFRARED RAYS ON SUBSTRATE UPPER SURFACE
H2O2 DISCHARGE FLOW RATE (SUBSTRATE UPPER SURFACE)
H2O2 LIQUID LANDING POSITION (SUBSTRATE UPPER SURFACE)
WARM WATER DISCHARGE (SUBSTRATE LOWER SURFACE)
WARM WATER LANDING POSITION (SUBSTRATE LOWER SURFACE)
O
O
ON
OFF
O
PERIPHERAL EDGE
INTERMEDIATE
CENTRAL
ON
OFF
PERIPHERAL EDGE
INTERMEDIATE
CENTRAL
TIME
V1
V2
V3
S2
S4
S3
S5
S6
S7

FIG. 15

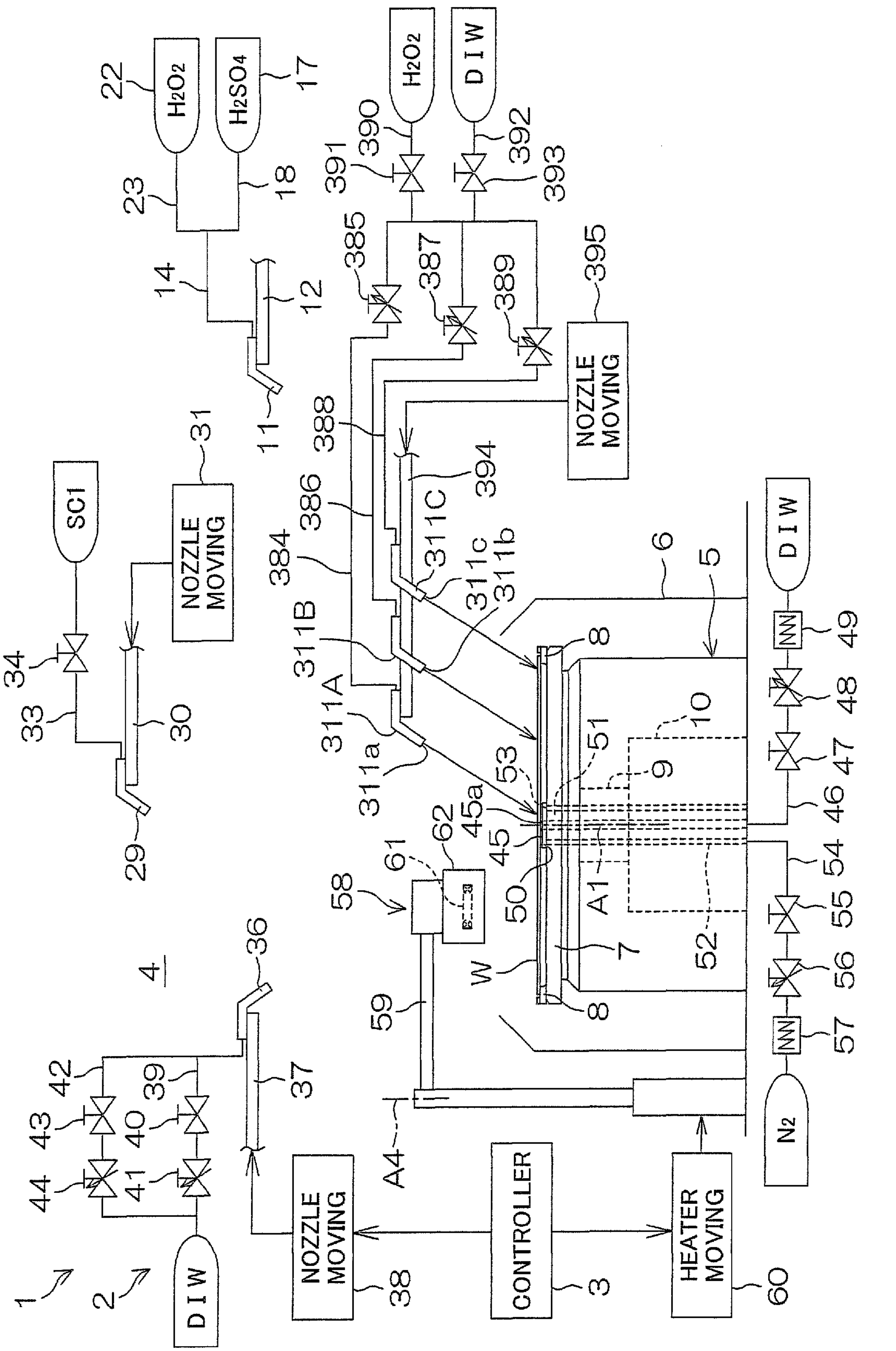

H2O2
H2SO4
H2O2
D I W
SC1
NOZZLE MOVING
NOZZLE MOVING
NOZZLE MOVING
D I W
D I W
N2
CONTROLLER
HEATER MOVING

FIG. 16A

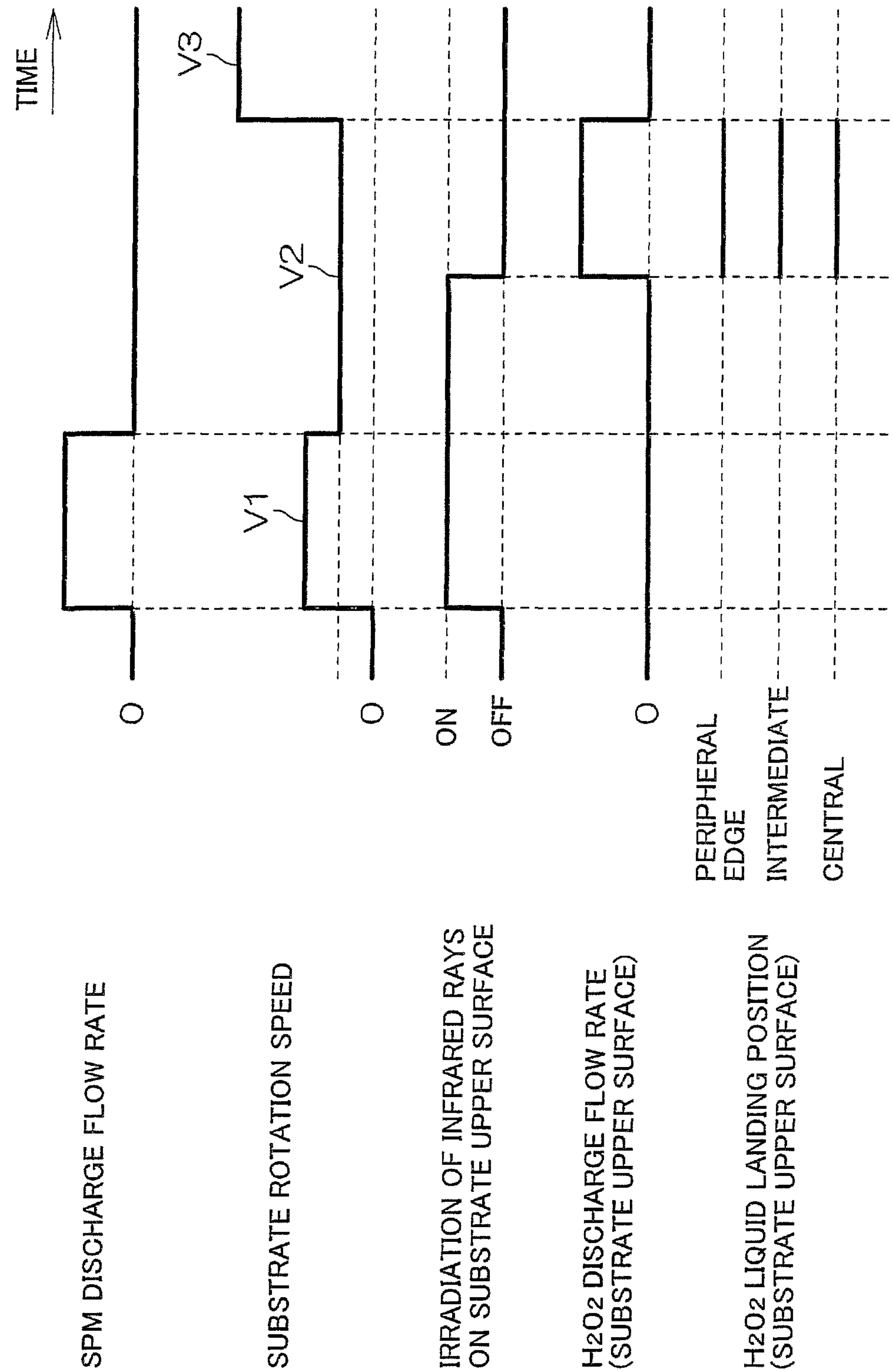

TIME
SPM DISCHARGE FLOW RATE
O
SUBSTRATE ROTATION SPEED
V1
V2
V3
O
IRRADIATION OF INFRARED RAYS ON SUBSTRATE UPPER SURFACE
ON
OFF
H2O2 DISCHARGE FLOW RATE (SUBSTRATE UPPER SURFACE)
O
H2O2 LIQUID LANDING POSITION (SUBSTRATE UPPER SURFACE)
PERIPHERAL EDGE
INTERMEDIATE
CENTRAL

FIG. 16B

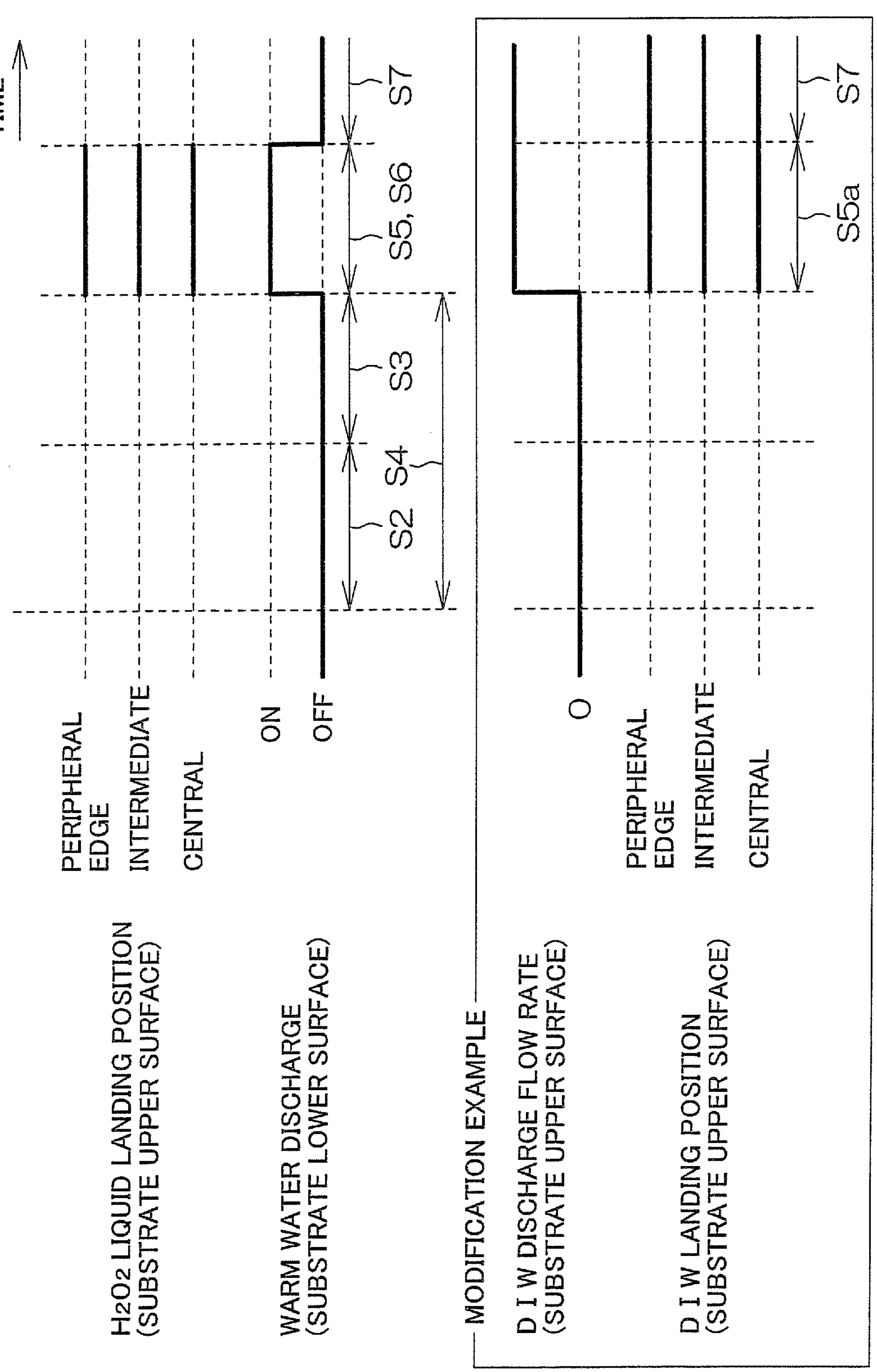

TIME
H_2O_2 LIQUID LANDING POSITION (SUBSTRATE UPPER SURFACE)
PERIPHERAL EDGE
INTERMEDIATE
CENTRAL
WARM WATER DISCHARGE (SUBSTRATE LOWER SURFACE)
ON
OFF
S2
S4
S3
S5, S6
S7
MODIFICATION EXAMPLE
D I W DISCHARGE FLOW RATE (SUBSTRATE UPPER SURFACE)
O
D I W LANDING POSITION (SUBSTRATE UPPER SURFACE)
PERIPHERAL EDGE
INTERMEDIATE
CENTRAL
S5a
S7

FIG. 17

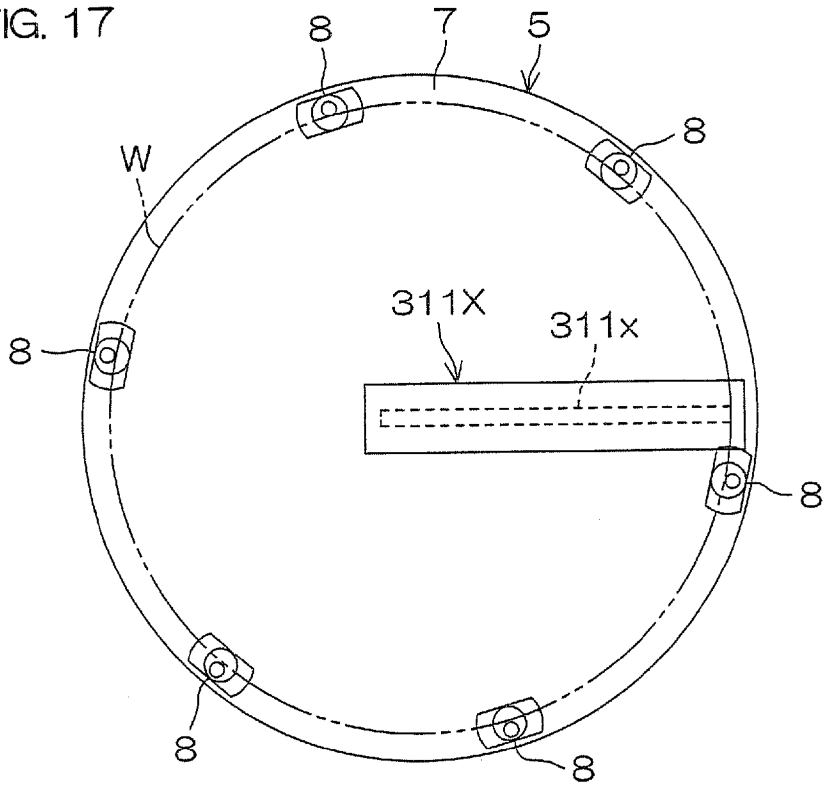


FIG. 18

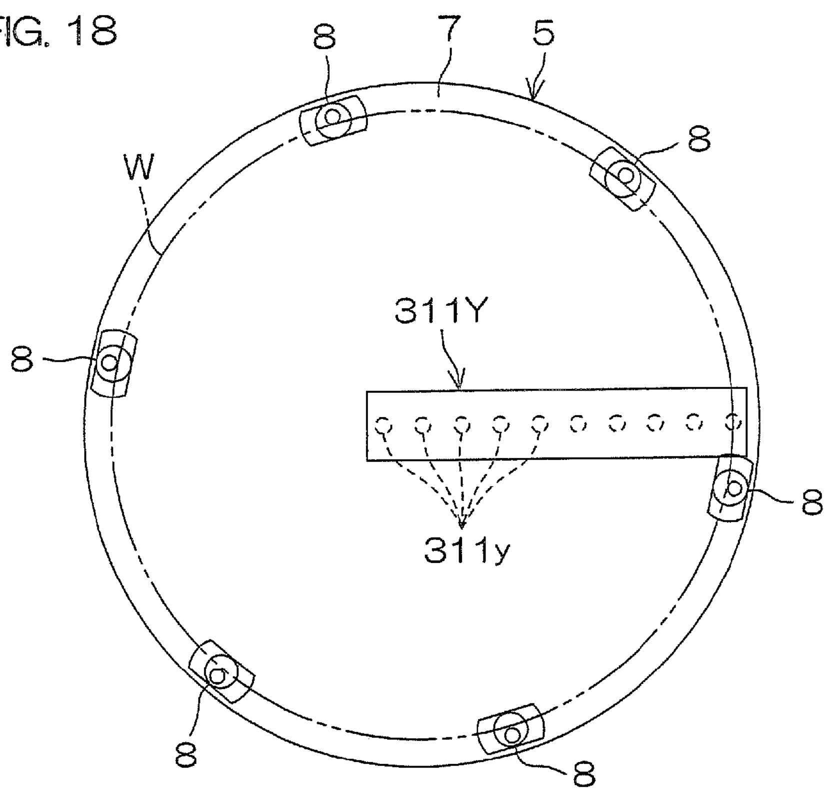


FIG. 19

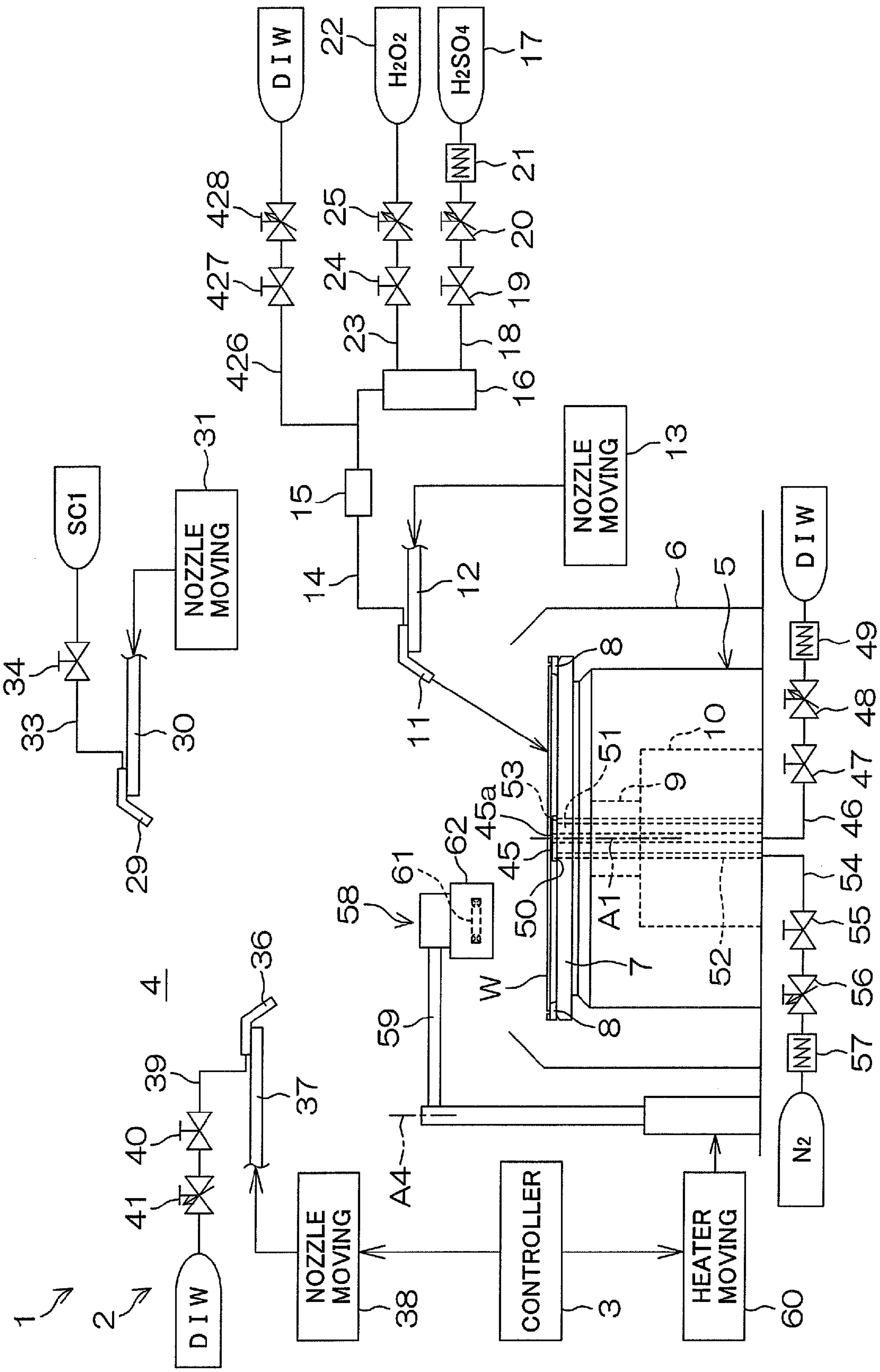

DIW
H_2O_2
H_2SO_4
SC1
NOZZLE MOVING
NOZZLE MOVING
NOZZLE MOVING
CONTROLLER
HEATER MOVING
DIW
N_2
DIW
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
29
30
31
33
34
36
37
38
39
40
41
45
45a
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
426
427
428
A1
A4
W

FIG. 20

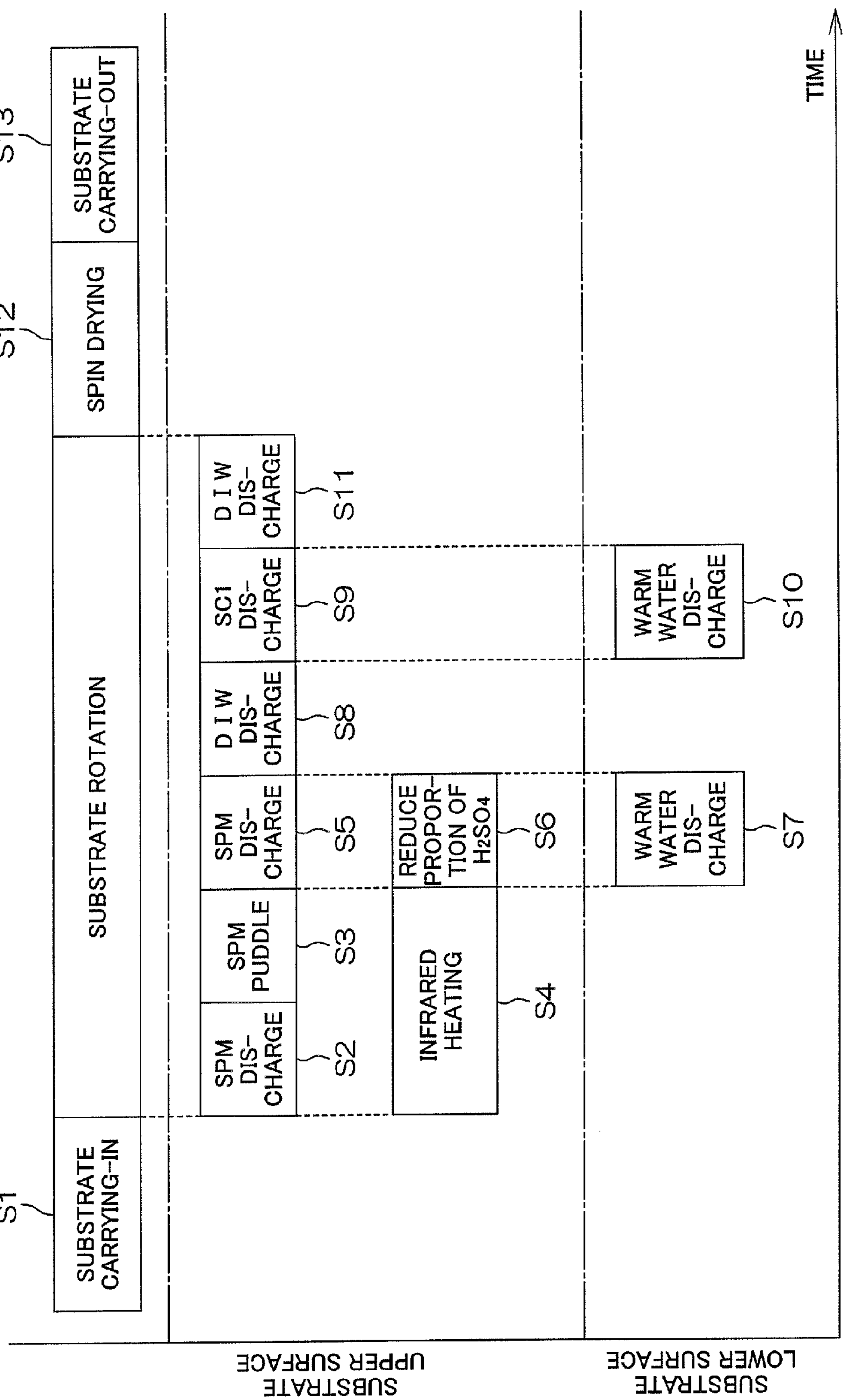
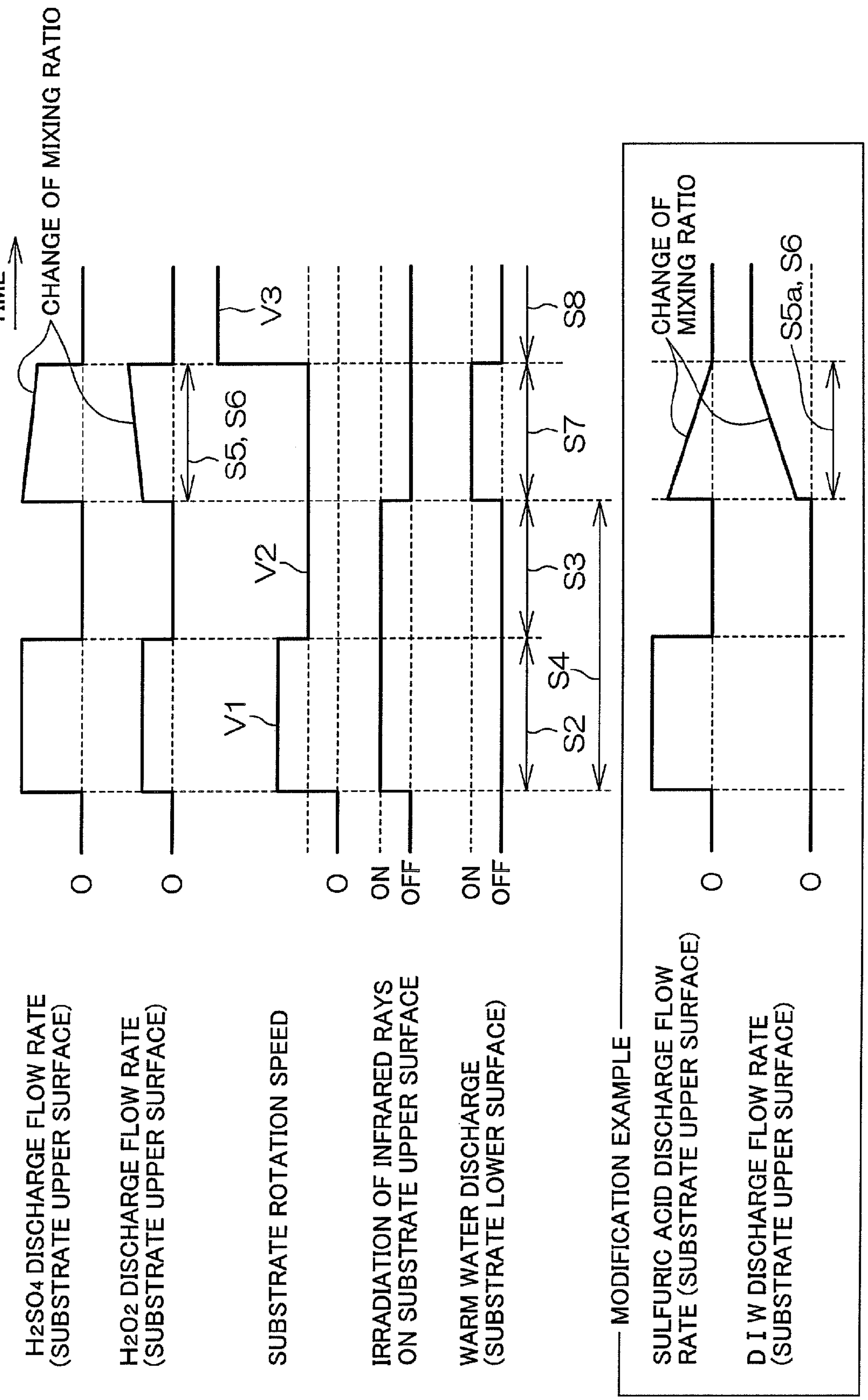

S1
SUBSTRATE CARRYING-IN
SUBSTRATE ROTATION
S12
SPIN DRYING
S13
SUBSTRATE CARRYING-OUT
SPM DIS-CHARGE
S2
SPM PUDDLE
S3
SPM DIS-CHARGE
S5
D I W DIS-CHARGE
S8
SC1 DIS-CHARGE
S9
D I W DIS-CHARGE
S11
INFRARED HEATING
S4
REDUCE PROPOR-TION OF H2SO4
S6
WARM WATER DIS-CHARGE
S7
WARM WATER DIS-CHARGE
S10
TIME
SUBSTRATE UPPER SURFACE
SUBSTRATE LOWER SURFACE

FIG. 21


TIME
CHANGE OF MIXING RATIO
H_2SO_4 DISCHARGE FLOW RATE (SUBSTRATE UPPER SURFACE)
H_2O_2 DISCHARGE FLOW RATE (SUBSTRATE UPPER SURFACE)
SUBSTRATE ROTATION SPEED
IRRADIATION OF INFRARED RAYS ON SUBSTRATE UPPER SURFACE
WARM WATER DISCHARGE (SUBSTRATE LOWER SURFACE)
0
0
0
ON
OFF
ON
OFF
V1
V2
V3
S5, S6
S2
S4
S3
S7
S8
MODIFICATION EXAMPLE
SULFURIC ACID DISCHARGE FLOW RATE (SUBSTRATE UPPER SURFACE)
D I W DISCHARGE FLOW RATE (SUBSTRATE UPPER SURFACE)
0
0
CHANGE OF MIXING RATIO
S5a, S6

SUBSTRATE PROCESSING METHOD AND SUBSTRATE PROCESSING APPARATUS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a substrate processing apparatus and a substrate processing method for processing a substrate. Examples of substrates to be processed include semiconductor wafers, substrates for liquid crystal displays, substrates for plasma displays, substrates for FEDs (field emission displays), substrates for optical disks, substrates for magnetic disks, substrates for magneto-optical disks, substrates for photomasks, ceramic substrates, substrates for solar cells, etc.

2. Description of Related Art

In a manufacturing process for a semiconductor device or a liquid crystal display device, etc., processing liquids having different temperatures may be supplied successively to a substrate while rotating the substrate by a spin chuck. For example, Japanese Patent Application Publication No. 2009-238862 discloses that after supplying SPM (sulfuric acid-hydrogen peroxide mixture) having high temperature to an upper surface of a rotating substrate, DIW (deionized water) having ordinary temperature is supplied to the upper surface of the substrate that is covered with the SPM to rinse off the SPM attached to the upper surface of the substrate.

When a high-temperature SPM or other high-temperature processing liquid is supplied to a substrate, the substrate itself becomes high in temperature. When in the state where the substrate is covered with the high-temperature processing liquid, the supplying of an ordinary temperature DIW or other low-temperature processing liquid is started, the temperature of the substrate decreases suddenly and rapidly at a liquid landing position of the low-temperature processing liquid and at positions in a vicinity of the liquid landing position (hereinafter referred to as a “liquid landing position vicinity region”). Stress that contracts the substrate thus arises in the liquid landing position vicinity region and the substrate deforms so as to be warped or undulated due to a temperature difference between the liquid landing position vicinity region and another region that is in a high-temperature state. Although when the low-temperature processing liquid spreads sufficiently across the substrate, the temperature differences between respective portions of the substrate decrease and such deformation is resolved, the state in which the substrate is deformed is sustained until then.

With a clamping type spin chuck, a plurality of chuck pins are pressed against a peripheral edge portion of a substrate. When the substrate deforms in the state where the plurality of chuck pins are pressed against the peripheral edge portion of the substrate, the pressing pressures applied to the substrate by the respective chuck pins change and the stability of substrate holding by the spin chuck may decrease. Also, with a vacuum type spin chuck, a lower surface of a substrate is suctioned onto an upper surface of a spin base (suction base). When the substrate deforms in the state where the lower surface of the substrate is suctioned onto the upper surface of the spin base, the closely contacting state of the lower surface of the substrate and the upper surface of the spin base changes and the stability of substrate holding by the spin chuck may decrease.

In the abovementioned publication, it is disclosed that the SPM having high temperature (for example, 150° C.) and DIW having ordinary temperature (for example, 25° C.) are supplied to the substrate. The supplying of the DIW as the low-temperature processing liquid may thus be started in a state where there is a temperature difference of not less than 100° C. between the substrate and the DIW. The present inventors have confirmed that the deformation of the substrate can occur not only when the temperature difference between the substrate and the low-temperature processing liquid is not less than 100° C. but can also occur when the temperature difference is less than 100° C. (for example, at 60° C.). The deformation of the substrate can thus occur not only when the high-temperature SPM and the ordinary-temperature DIW are supplied successively but can also occur when other processing liquids with temperature difference are supplied successively to the substrate.

SUMMARY OF THE INVENTION

An object of the present invention is to suppress localized temperature change of a substrate at the start of supplying of a processing liquid.

A preferred embodiment of the present invention provides a substrate processing method including a chemical liquid supplying step of supplying a chemical liquid having a first temperature to a major surface of a substrate, a rinse liquid supplying step of supplying, after the chemical liquid supplying step, a rinse liquid having a second temperature lower than the first temperature to the major surface of the substrate to rinse off the liquid remaining on the substrate, and a reaction liquid supplying step of supplying, after the chemical liquid supplying step and before the rinse liquid supplying step, a reaction liquid, causing an exothermic reaction upon mixing with the chemical liquid and having a liquid temperature lower than the first temperature and not less than the second temperature, to the major surface of the substrate in a state where the chemical liquid supplied to the substrate in the chemical liquid supplying step remains on the substrate. The major surface of the substrate may be a front surface on which a device is formed or may be a rear surface at the opposite side of the front surface.

With this method, the chemical liquid having the first temperature (the temperature of the chemical liquid before being supplied to the substrate) is supplied to the major surface of the substrate. The reaction liquid is then supplied to the major surface of the substrate in the state where the chemical liquid remains on the substrate. The reaction liquid supplied to the substrate mixes with the chemical liquid remaining on the substrate. The proportion of the reaction liquid in the liquid remaining on the substrate (the liquid containing the chemical liquid and the reaction liquid) thus increases and the concentration of the chemical liquid decreases. The rinse liquid having the second temperature (the temperature of the rinse liquid before being supplied to the substrate) lower than the first temperature is supplied to the major surface of the substrate after the reaction liquid has been supplied to the substrate. The liquid remaining on the substrate is thereby rinsed off.

When the supplying of the reaction liquid is started, the temperature of the substrate approaches the temperature of the reaction liquid. The temperature of the reaction liquid before being supplied to the substrate is lower than the temperature (first temperature) of the chemical liquid and not less than the temperature (second temperature) of the rinse liquid. Upon mixing with the chemical liquid, the reaction liquid causes an exothermic reaction in the chemical liquid. Therefore, when the reaction liquid is supplied to the major surface of the substrate in the state where the chemical liquid remains on the substrate, the exothermic reaction occurs at the liquid landing position of the reaction liquid and at positions in the vicinity of the liquid landing position so that the temperature decrease amount of the substrate is reduced in the liquid landing position vicinity region. The temperature of the substrate thus approaches the temperature of the reaction liquid gradually. Sudden and rapid temperature decrease of the substrate can thus be suppressed to reduce the amount of deformation of the substrate in comparison to a case where the rinse liquid having the second temperature lower than the first temperature is supplied to the substrate in succession to the supplying of the chemical liquid.

In the preferred embodiment of the present invention, the reaction liquid supplying step may include a supply starting step of starting the supplying of the reaction liquid to the major surface of the substrate at an intermediate portion, between a central portion and a peripheral edge portion, in a state where the entire major surface of the substrate that is rotating is covered by the chemical liquid, and a liquid landing position moving step of moving, after the supply starting step, a liquid landing position of the reaction liquid with respect to the major surface of the substrate from the intermediate portion to the central portion in a state where the entire major surface of the substrate that is rotating is covered by the chemical liquid and the reaction liquid.

With this method, the supplying of the reaction liquid to the major surface of the substrate is started at the intermediate portion, between the central portion and the peripheral edge portion, in the state where the substrate is rotating and the entire major surface of the substrate is covered by the chemical liquid. In succession, the liquid landing position of the reaction liquid with respect to the major surface of the substrate is moved from the intermediate portion to the central portion. The centrifugal force due to the rotation of the substrate is applied to the reaction liquid and the reaction liquid supplied to the substrate thus flows outward to the peripheral edge portion along the major surface of the substrate. The reaction liquid is thereby supplied to the entire major surface of the substrate. The proportion of the reaction liquid in the liquid film covering the entire major surface of the substrate thus increases gradually and the temperatures of the respective portions of the substrate approach the temperature of the reaction liquid.

The temperature difference between the substrate and the reaction liquid is greatest when the supplying of the reaction liquid is started. The circumferential speed (speed in the rotation direction) at the major surface intermediate portion of the substrate is greater than the circumferential speed at the major surface central portion of the substrate, and therefore, the supply flow rate of the reaction liquid per unit area is lower than in a case where the supplying of the reaction liquid is started at the major surface central portion of the substrate. The temperatures of the substrate and the chemical liquid at the liquid landing position can thus be suppressed or prevented from decreasing suddenly and rapidly due to the supplying of a large amount of the reaction liquid. Further, the reaction liquid that lands on the major surface central portion of the substrate is expelled to the periphery of the substrate via the major surface peripheral edge portion of the substrate and therefore the retention time of the reaction liquid on the substrate is longer than in a case where the supplying of the reaction liquid is started at the major surface peripheral edge portion of the substrate. The reaction liquid can thus be used efficiently.

In the preferred embodiment of the present invention, the reaction liquid supplying step may include a step of discharging the reaction liquid in a discharge direction that is inclined with respect to the major surface of the substrate.

With this method, the reaction liquid is discharged toward the major surface of the substrate in the direction that is inclined with respect to the major surface of the substrate. The reaction liquid is thus made obliquely incident on the major surface of the substrate. The impact when the reaction liquid lands on the substrate is thus smaller than in a case where the reaction liquid is made perpendicularly incident on the major surface of the substrate. In a case where a pattern is formed on the major surface of the substrate, if the impact applied to the substrate is reduced, the impact applied to the pattern is reduced. Occurrence of damage, such as pattern collapse, etc., can thus be suppressed or prevented.

In the preferred embodiment of the present invention, the reaction liquid supplying step may include a step of discharging the reaction liquid in the discharge direction that is inclined with respect to the major surface of the substrate so as to be positioned closer to the center of the substrate as the discharge direction approaches the major surface of the substrate.

With this method the reaction liquid is discharged toward the major surface of the substrate in the direction that is inclined with respect to the major surface of the substrate so as to be positioned closer to the center of the substrate as the discharge direction approaches the major surface of the substrate. The reaction liquid thus mainly flows inwardly (toward the center of the substrate) from the liquid landing position along the substrate. The reaction liquid can thus be spread to a region further inward than the liquid landing position in a shorter time than in a case where the reaction liquid is discharged in the direction perpendicular to the major surface of the substrate or in a case where the reaction liquid is discharged outwardly with respect to the major surface of the substrate. Further, the flow rate of the reaction liquid flowing inwardly from the liquid landing position is increased in comparison to these cases and the retention time of the reaction liquid on the substrate is thus increased. The reaction liquid can thus be used efficiently.

In the preferred embodiment of the present invention, the chemical liquid supplied to the substrate in the chemical liquid supplying step may be a mixed liquid of a reaction chemical liquid having a liquid temperature lower than the first temperature and not less than the second temperature and a heat generating chemical liquid that generates heat upon mixing with the reaction chemical liquid. The reaction liquid supplying step may include a step of supplying the reaction chemical liquid as the reaction liquid to the major surface of the substrate.

With this method, the reaction chemical liquid having a liquid temperature lower than the first temperature and not less than the second temperature is mixed with the heat generating chemical liquid that generates heat upon mixing with the reaction chemical liquid. The heat generating chemical liquid and the reaction chemical liquid are thus raised in temperature to the first temperature by the heat generation of the heat generating chemical liquid to form the chemical liquid having the first temperature. The reaction chemical liquid as the reaction liquid is supplied to the major surface of the substrate in the state where the chemical liquid remains on the substrate. The reaction chemical liquid as the reaction liquid thus mixes with the heat generating chemical liquid contained in the chemical liquid on the substrate and an exothermic reaction occurs at the liquid landing position of the reaction liquid and at positions in its vicinity. The temperature decrease amount of the substrate in the liquid landing position vicinity region is thus decreased. Further, a chemical liquid of the same type as a component chemical liquid (the reaction chemical liquid in the present case) contained in the chemical liquid, that is, a liquid with a high affinity to the chemical liquid is used as the reaction liquid and therefore the chemical liquid and the reaction liquid can be mixed efficiently.

In the preferred embodiment of the present invention, the reaction liquid supplying step may include a step of discharging the reaction liquid toward the major surface of the substrate in a state where the substrate is rotating at a rotation speed that is higher than the rotation speed of the substrate in at least a portion of a period between the start of supplying of the chemical liquid to the substrate and the start of supplying of the reaction liquid to the substrate.

With this method, the reaction liquid is discharged toward the major surface of the substrate in a state where the substrate is rotating at the relatively high rotation speed, that is, the rotation speed that is higher than the rotation speed of the substrate in at least a portion of a period between the start of supplying of the chemical liquid to the substrate and the start of supplying of the reaction liquid to the substrate. The centrifugal force applied to the liquid attached to the substrate thus increases. The chemical liquid remaining on the substrate is thus spun off rapidly to the periphery of the substrate and the reaction liquid supplied to the substrate is spread across the entire major surface of the substrate rapidly. The temperature of the entire major surface of the substrate thus decreases uniformly so that the deformation of the substrate due to temperature difference can be suppressed or prevented.

In the preferred embodiment of the present invention, the reaction liquid supplying step may include a step of discharging the reaction liquid simultaneously toward the major surface central portion, the major surface intermediate portion, and the major surface peripheral edge portion of the substrate in the state where the substrate is rotating.

With this method, in the state where the substrate is rotating, the reaction liquid is discharged simultaneously toward a plurality of positions within the major surface of the substrate that respectively differ in distance from the center of the substrate. More specifically, the reaction liquid is discharged simultaneously toward the major surface central portion, the major surface intermediate portion, and the major surface peripheral edge portion of the substrate. Therefore, when the substrate rotates by one turn or more, the reaction liquid is spread across the entire major surface of the substrate. The reaction liquid is thus spread across the entire major surface of the substrate in a short time and the temperature of the entire major surface of the substrate decreases uniformly. Deformation of the substrate due to temperature difference can thereby be suppressed or prevented.

In the preferred embodiment of the present invention, the reaction liquid supplying step may include a step of making the reaction liquid land simultaneously on the entirety of a region, which is within the major surface of the substrate and includes the radius of the substrate, in the state where the substrate is rotating.

With this method, the reaction liquid is discharged simultaneously toward the entirety of the region that is within the major surface of the substrate and includes the radius of the substrate and lands simultaneously on the entire region in the state where the substrate is rotating. That is, the reaction liquid is supplied simultaneously to the entire region that is continuous in the radial direction of the substrate from the center of the substrate to the peripheral edge of the substrate. Therefore when the substrate rotates by one turn or more, the reaction liquid is spread across the entire major surface of the substrate. The reaction liquid is thus spread across the entire major surface of the substrate in a short time and the temperature of the entire major surface of the substrate decreases uniformly. Deformation of the substrate due to temperature difference can thereby be suppressed or prevented.

The substrate processing method may further include a heating step of heating, before the reaction liquid supplying step, the substrate and the chemical liquid at a heating temperature higher than the first temperature in the state in which the chemical liquid supplied to the substrate in the chemical liquid supplying step remains on the substrate. In this case, the heating step may include an infrared heating step of heating the substrate and the chemical liquid at the heating temperature by an infrared heater facing the major surface of the substrate.

With this method, the temperatures of the substrate and the chemical liquid rise to the heating temperature higher than the temperature (first temperature) of the chemical liquid before being supplied to the substrate, and the temperature difference between the substrate before the supplying of the reaction liquid and the rinse liquid is increased further. The arising of a large temperature difference within the substrate due to localized decrease of the substrate temperature when the rinse liquid is supplied to the substrate can thus be suppressed or prevented by supplying the reaction liquid to the substrate before supplying the rinse liquid. The amount of deformation of the substrate can thereby be reduced.

Another preferred embodiment of the present invention provides a substrate processing apparatus including a substrate holding unit holding and rotating a substrate, a chemical liquid supplying unit discharging a chemical liquid having a first temperature toward a major surface of the substrate held by the substrate holding unit, a rinse liquid supplying unit discharging a rinse liquid having a second temperature lower than the first temperature toward the major surface of the substrate held by the substrate holding unit, a reaction liquid supplying unit discharging a reaction liquid, being of a liquid temperature lower than the first temperature and not less than the second temperature and causing an exothermic reaction upon mixing with the chemical liquid, toward the major surface of the substrate held by the substrate holding unit, and a controller controlling the substrate holding unit, the chemical liquid supplying unit, the rinse liquid supplying unit, and the reaction liquid supplying unit.

The controller executes a chemical liquid supplying step of supplying the chemical liquid having the first temperature to the major surface of the substrate, a rinse liquid supplying step of supplying, after the chemical liquid supplying step, the rinse liquid having the second temperature to the major surface of the substrate to rinse off the liquid remaining on the substrate, and a reaction liquid supplying step of supplying, after the chemical liquid supplying step and before the rinse liquid supplying step, the reaction liquid of the liquid temperature lower than the first temperature and not less than the second temperature to the major surface of the substrate in a state where the chemical liquid supplied to the substrate in the chemical liquid supplying step remains on the substrate. With this arrangement, the respective steps of the substrate processing method described above are executed by the controller controlling the substrate processing apparatus. The same effects as the effects described above can thus be exhibited.

Yet another preferred embodiment of the present invention provides a substrate processing method including a chemical liquid supplying step of supplying a chemical liquid having a first temperature to a major surface of a substrate, a rinse liquid supplying step of supplying, after the chemical liquid supplying step, a rinse liquid having a second temperature lower than the first temperature to the major surface of the substrate to rinse off the liquid remaining on the substrate, a reaction liquid supplying step of discharging, after the chemical liquid supplying step and before the rinse liquid supplying step, a reaction-liquid-containing liquid, which contains, at least at the start of discharge, a reaction liquid, causing an exothermic reaction upon mixing with the chemical liquid supplied to the substrate in the chemical liquid supplying step, and a heat generating liquid, generating heat upon mixing with the reaction liquid, and has a liquid temperature not more than the first temperature and not less than the second temperature, toward the major surface of the substrate in a state where the chemical liquid supplied to the substrate in the chemical liquid supplying step remains on the substrate, and a reaction liquid concentration changing step of reducing, in parallel to the reaction liquid supplying step, the proportion of the heat generating liquid contained in the reaction-liquid-containing liquid discharged toward the substrate to decrease the temperature of the reaction-liquid-containing liquid discharged toward the substrate to lower than the temperature of the reaction-liquid-containing liquid at the start of discharge.

With this method, the chemical liquid having the first temperature (the temperature of the chemical liquid before being supplied to the substrate) is supplied to the major surface of the substrate. The reaction-liquid-containing liquid is then supplied to the major surface of the substrate in the state where the chemical liquid remains on the substrate. The reaction-liquid-containing liquid supplied to the substrate mixes with the chemical liquid remaining on the substrate. The proportion of the reaction-liquid-containing liquid in the liquid remaining on the substrate thus increases and the concentration of the chemical liquid decreases. The rinse liquid having the second temperature (the temperature of the rinse liquid before being supplied to the substrate) lower than the first temperature is supplied to the major surface of the substrate after the reaction-liquid-containing liquid has been supplied to the substrate. The liquid remaining on the substrate (the liquid containing the chemical liquid and the reaction-liquid-containing liquid) is thereby rinsed off.

The reaction-liquid-containing liquid at the start of discharge is a mixed liquid formed by mixing the reaction liquid and the heat generating liquid. The reaction liquid is a liquid that causes an exothermic reaction upon mixing with the chemical liquid. The heat generating liquid is a liquid that generates heat upon mixing with the reaction liquid. By being mixed with the heat generating liquid, the reaction liquid is heated by the heat generating liquid.

When the supplying of the reaction-liquid-containing liquid is started, the temperature of the substrate approaches the temperature of the reaction-liquid-containing liquid. The temperature of the reaction-liquid-containing liquid before being supplied to the substrate is not more than the temperature (first temperature) of the chemical liquid and not less than the temperature (second temperature) of the rinse liquid. Upon mixing with the chemical liquid, the reaction-liquid-containing liquid causes an exothermic reaction. Therefore, when the reaction-liquid-containing liquid is supplied to the major surface of the substrate in the state where the chemical liquid remains on the substrate, the exothermic reaction occurs at the liquid landing position of the reaction-liquid-containing liquid and at positions in the vicinity of the liquid landing position so that the temperature decrease amount of the substrate is reduced in the liquid landing position vicinity region. The temperature of the substrate thus approaches the temperature of the reaction-liquid-containing liquid gradually.

Further, the proportion of the heat generating liquid contained in the reaction-liquid-containing liquid decreases from that at the start of discharge of the reaction-liquid-containing liquid so that the proportion of the reaction liquid having lower temperature than the heat generating liquid increases and consequently, the temperature of the reaction-liquid-containing liquid decreases. Therefore, the reaction-liquid-containing liquid having lower temperature than the reaction-liquid-containing liquid at the start of discharge is supplied to the major surface of the substrate and the temperature of the reaction-liquid-containing liquid approaches the temperature (second temperature) of the rinse liquid. The temperature decrease of the substrate in the liquid landing position vicinity region is thus made even more gradual. Sudden and rapid temperature decrease of the substrate can thus be suppressed to reduce the amount of deformation of the substrate in comparison to a case where the rinse liquid is supplied to the substrate in succession to the supplying of the chemical liquid.

In the yet other preferred embodiment of the present invention, the reaction liquid concentration changing step may include a step of changing a mixing ratio of the reaction liquid and the heat generating liquid from a first mixing ratio, in which the proportion of the heat generating liquid is greater than the proportion of the reaction liquid, to a second mixing ratio, in which the proportion of the heat generating liquid is less than the proportion of the reaction liquid, to reduce the proportion of the heat generating liquid contained in the reaction-liquid-containing liquid discharged toward the substrate and decrease the temperature of the reaction-liquid-containing liquid discharged toward the substrate to lower than the temperature of the reaction-liquid-containing liquid at the start of discharge of itself.

With this method, the reaction-liquid-containing liquid, in which the proportion of the heat generating liquid is large, is discharged toward the major surface of the substrate. Thereafter, the proportion of the heat generating liquid contained in the reaction-liquid-containing liquid is reduced. The temperature of the reaction-liquid-containing liquid that is discharged toward the substrate thus decreases greatly gradually. Therefore, even when the temperature difference of the chemical liquid and the rinse liquid is large, that is, even when the difference between the first temperature and the second temperature is large, the temperature of the substrate can be made to approach the temperature of the rinse liquid gradually and yet uniformly. Deformation of the substrate due to temperature difference can thereby be suppressed or prevented.

In the yet other preferred embodiment of the present invention, the reaction liquid concentration changing step may include a step of reducing the proportion of the heat generating liquid contained in the reaction-liquid-containing liquid discharged toward the substrate to zero to decrease the temperature of the reaction-liquid-containing liquid discharged toward the substrate to lower than the temperature of the reaction-liquid-containing liquid at the start of discharge.

With this method, the proportion of the heat generating liquid contained in the reaction-liquid-containing liquid is reduced to zero. The heat generating liquid contained in the reaction-liquid-containing liquid is thus eliminated and only the reaction liquid is discharged toward the substrate. The temperature of the reaction-liquid-containing liquid that is discharged toward the substrate thus decreases greatly gradually and the temperature change amount of the reaction-liquid-containing liquid increases. Therefore, even when the temperature difference of the chemical liquid and the rinse liquid is large, the temperature of the substrate can be made to approach the temperature of the rinse liquid gradually and yet uniformly.

In the yet other preferred embodiment of the present invention, the chemical liquid supplied to the substrate in the chemical liquid supplying step may be a mixed liquid of a reaction chemical liquid and a heat generating chemical liquid that is higher in temperature than the reaction chemical liquid and generates heat upon mixing with the reaction chemical liquid, and the reaction-liquid-containing liquid at the start of discharge may be a mixed liquid of the reaction chemical liquid as the reaction liquid and the heat generating chemical liquid as the heat generating liquid.

With this method, the chemical liquid having the first temperature is formed by the heat generating chemical liquid (for example, sulfuric acid) having higher temperature than the reaction chemical liquid (for example, hydrogen peroxide water) being mixed at a predetermined mixing ratio with the reaction chemical liquid. Similarly, the reaction-liquid-containing liquid is formed by the heat generating chemical liquid being mixed at a predetermined mixing ratio with the reaction chemical liquid. The reaction-liquid-containing liquid that contains the heat generating chemical liquid and the reaction chemical liquid is discharged toward the substrate in the state where the chemical liquid is remaining on the substrate. Therefore, the reaction chemical liquid contained in the reaction-liquid-containing liquid mixes with the heat generating chemical liquid contained in the chemical liquid remaining on the substrate and the exothermic reaction occurs at the liquid landing position of the reaction-liquid-containing liquid and at positions in its vicinity. The temperature decrease amount of the substrate is thus reduced in the liquid landing position vicinity region. Further, a liquid containing the same component chemical liquid as the chemical liquid, that is, a liquid with a high affinity to the chemical liquid is used as the reaction-liquid-containing liquid and therefore the chemical liquid and the reaction-liquid-containing liquid can be mixed efficiently.

In the yet other preferred embodiment of the present invention, the chemical liquid supplied to the substrate in the chemical liquid supplying step may be a mixed liquid of a reaction chemical liquid and a heat generating chemical liquid that is higher in temperature than the reaction chemical liquid and generates heat upon mixing with the reaction chemical liquid. The reaction-liquid-containing liquid at the start of discharge may be a mixed liquid of the reaction liquid that causes the exothermic reaction upon mixing with the chemical liquid supplied to the substrate in the chemical liquid supplying step and a heat-generating-chemical-liquid-containing liquid containing the heat generating chemical liquid as the heat generating liquid.

With this method, the chemical liquid having the first temperature is formed by the heat generating chemical liquid (for example, sulfuric acid) having higher temperature than the reaction chemical liquid (for example, hydrogen peroxide water) being mixed at a predetermined mixing ratio with the reaction chemical liquid. Similarly, the reaction-liquid-containing liquid is generated by the heat-generating-liquid-containing liquid, which contains the heat generating chemical liquid as the heat generating liquid, being mixed at a predetermined mixing ratio with the reaction liquid (for example, pure water). The reaction-liquid-containing liquid that contains the reaction liquid and the heat-generating-chemical-liquid-containing liquid is discharged toward the substrate in the state where the chemical liquid is remaining on the substrate. Therefore, the reaction liquid contained in the reaction-liquid-containing liquid mixes with the chemical liquid remaining on the substrate and the exothermic reaction occurs at the liquid landing position of the reaction-liquid-containing liquid and at positions in its vicinity. The temperature decrease amount of the substrate is thus reduced in the liquid landing position vicinity region. Further, a liquid containing the same component chemical liquid as the chemical liquid is used as the reaction-liquid-containing liquid and therefore the chemical liquid and the reaction-liquid-containing liquid can be mixed efficiently.

In the yet other preferred embodiment of the present invention, the reaction liquid may be a liquid that is the same in composition as the rinse liquid supplied to the substrate in the rinse liquid supplying step and causes an exothermic reaction upon mixing with the chemical liquid supplied to the substrate in the chemical liquid supplying step. The reaction liquid concentration changing step may include a step of reducing the proportion of the heat generating liquid contained in the reaction-liquid-containing liquid discharged toward the substrate to zero to decrease the temperature of the reaction-liquid-containing liquid discharged toward the substrate to lower than the temperature of the reaction-liquid-containing liquid at the start of discharge and make the composition of the reaction-liquid-containing liquid discharged toward the substrate match the composition of the rinse liquid supplied to the substrate in the rinse liquid supplying step.

With this method, the reaction liquid contained in the reaction-liquid-containing liquid is the same in composition as the rinse liquid and the proportion of the heat generating liquid contained in the reaction-liquid-containing liquid is reduced to zero. The heat generating liquid contained in the reaction-liquid-containing liquid is thus eliminated and only the reaction liquid, that is, the same type of liquid as the rinse liquid is discharged toward the substrate. Therefore not only does the temperature of the reaction-liquid-containing liquid decrease greatly gradually but the affinity of the liquid, remaining on the substrate before the rinse liquid supplying step, and the rinse liquid is increased as well. The liquid remaining on the substrate can thus be rinsed off smoothly by supplying the rinse liquid after supplying the reaction-liquid-containing liquid.

Yet another preferred embodiment of the present invention provides a substrate processing apparatus including a substrate holding unit holding and rotating a substrate, a chemical liquid supplying unit discharging a chemical liquid having a first temperature toward a major surface of the substrate held by the substrate holding unit, a rinse liquid supplying unit discharging a rinse liquid having a second temperature lower than the first temperature toward the major surface of the substrate held by the substrate holding unit, a reaction liquid supplying unit including a reaction liquid nozzle, discharging a reaction-liquid-containing liquid, which is formed by mixing a reaction liquid, causing an exothermic reaction upon mixing with the chemical liquid, and a heat generating liquid, being higher in temperature than the reaction liquid and generating heat upon mixing with the reaction liquid, and has a liquid temperature not more than the first temperature and not less than the second temperature, toward the major surface of the substrate held by the substrate holding unit, and a concentration changing unit, changing the proportion of the heat generating liquid contained in the reaction-liquid-containing liquid discharged from the reaction liquid nozzle, and a controller controlling the substrate holding unit, the chemical liquid supplying unit, the rinse liquid supplying unit, and the reaction liquid supplying unit.

The controller executes a chemical liquid supplying step of supplying the chemical liquid having the first temperature to the major surface of a substrate, a rinse liquid supplying step of supplying, after the chemical liquid supplying step, the rinse liquid having the second temperature to the major surface of the substrate to rinse off the liquid remaining on the substrate, a reaction liquid supplying step of discharging, after the chemical liquid supplying step and before the rinse liquid supplying step, a reaction-liquid-containing liquid, which has a liquid temperature not more than the first temperature and not less than the second temperature, toward the major surface of the substrate in a state where the chemical liquid supplied to the substrate in the chemical liquid supplying step remains on the substrate, and a reaction liquid concentration changing step of reducing, in parallel to the reaction liquid supplying step, the proportion of the heat generating liquid contained in the reaction-liquid-containing liquid discharged toward the substrate to decrease the temperature of the reaction-liquid-containing liquid discharged toward the substrate to lower than the temperature of the reaction-liquid-containing liquid at the start of discharge. With this arrangement, the respective steps of the substrate processing method described above are executed by the controller controlling the substrate processing apparatus. The same effects as the effects described above can thus be exhibited.

The aforementioned and other objects, features, and effects of the present invention shall be clarified by the following description of preferred embodiments with reference to the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a schematic plan view of a substrate processing apparatus according to a first preferred embodiment of the present invention.

FIG. **2** is a horizontally-viewed schematic view of the interior of a chamber included in the substrate processing apparatus according to the first preferred embodiment of the present invention.

FIG. **3** is a schematic plan view of a spin base and an arrangement related thereto.

FIG. **4** is a vertical sectional view of an infrared heater.

FIG. **5** is a time chart in outline of a first processing example performed by a processing unit.

FIGS. **6**A and **6**B are a specific time chart of a portion of the first processing example.

FIGS. **7**A and **7**B are a specific time chart of a portion of a second processing example performed by the processing unit.

FIG. **8** is a specific time chart of a portion of a third processing example performed by the processing unit.

FIG. **9** is a specific time chart of a portion of a fourth processing example performed by the processing unit.

FIG. **10** is a plan view of a spin chuck according to a second preferred embodiment of the present invention.

FIG. **11** is a front view of the spin chuck according to the second preferred embodiment of the present invention.

FIG. **12** is a schematic plan view of a lower surface nozzle.

FIG. **13** is a schematic sectional view of the internal arrangement of the lower surface nozzle.

FIG. **14** is a specific time chart of a portion of a fifth processing example performed by the processing unit.

FIG. **15** is a horizontally-viewed schematic view of the interior of a chamber included in a substrate processing apparatus according to a third preferred embodiment of the present invention.

FIGS. **16**A and **16**B are a specific time chart of a portion of a sixth processing example performed by the processing unit.

FIG. **17** is a schematic plan view of a modification example of a reaction liquid nozzle.

FIG. **18** is a schematic plan view of another modification example of the reaction liquid nozzle.

FIG. **19** is a horizontally-viewed schematic view of the interior of a chamber included in a substrate processing apparatus according to a fourth preferred embodiment of the present invention.

FIG. **20** is a time chart in outline of a seventh processing example performed by a processing unit.

FIG. **21** is a specific time chart of a portion of the seventh processing example.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

FIG. **1** is a schematic plan view of a substrate processing apparatus **1** according to a first preferred embodiment of the present invention. FIG. **2** is a horizontally-viewed schematic view of the interior of a chamber **4** included in the substrate processing apparatus **1** according to the first preferred embodiment of the present invention. FIG. **3** is a schematic plan view of a spin base **7** and an arrangement related thereto. FIG. **4** is a vertical sectional view of an infrared heater **58**.

As shown in FIG. **1**, the substrate processing apparatus **1** is a single substrate processing type apparatus that processes a disk-shaped substrate W, such as a semiconductor wafer, etc., one by one. The substrate processing apparatus **1** includes a plurality of processing units **2**, each processing a substrate W using processing liquids and processing gases, a substrate transfer robot CR performing carrying-in and carrying-out of a substrate W with respect to the chamber **4** of each processing unit **2**, and a controller **3** controlling operations of devices and opening and closing of valves provided in the substrate processing apparatus **1**.

As shown in FIG. **2**, each processing unit **2** is a single substrate processing type unit. Each processing unit **2** includes the box-shaped chamber **4** that has an internal space, a spin chuck **5** holding a single substrate W in a horizontal attitude inside the chamber **4** and rotating the substrate W around a vertical substrate rotation axis A**1** passing through the center of the substrate W, a processing liquid supplying device supplying a processing liquid, such as a chemical liquid, a rinse liquid, etc., to the substrate W held by the spin chuck **5**, a heating device heating the substrate W, held by the spin chuck **5**, from above the substrate W, and a cylindrical cup **6** surrounding a periphery of the spin chuck **5** around the substrate rotation axis A**1**.

As shown in FIG. **2**, the spin chuck **5**, corresponding to being a substrate holding unit, includes a disk-shaped spin base **7** that is held in a horizontal attitude, a plurality of chuck pins **8** projecting upward from upper surface outer peripheral portions of the spin base **7**, and a chuck opening/closing mechanism (not shown) that opens and closes the plurality of chuck pins **8**. The spin chuck **5** further includes a spin shaft **9** extending downward along the substrate rotation axis A**1** from a central portion of the spin base **7**, and a spin motor **10** rotating the spin shaft **9** to rotate the spin base **7** and the chuck pins **8** around the substrate rotation axis A**1**.

As shown in FIG. **2**, the outer diameter of the spin base **7** is greater than the diameter of the substrate W. The center line of the spin base **7** is disposed along the substrate rotation axis A**1**. The plurality of chuck pins **8** are held by the spin base **7** at the outer peripheral portions of the spin base **7**. The plurality of chuck pins **8** are spaced apart by intervals in the circumferential direction (direction around the substrate rotation axis A**1**). Each chuck pin **8** is each capable of rotating around a vertical pin rotation axis with respect to the spin base **7** between a closed position at which the chuck pin **8** is pressed against a peripheral end surface of the substrate W and an open position at which the chuck pin **8** is separated from the peripheral end surface of the substrate W. The chuck opening/closing mechanism makes the chuck pins **8** rotate around the pin rotation axes.

The controller **3** controls the chuck opening/closing mechanism to switch the state of the plurality of chuck pins **8** between the closed state in which the plurality of chuck pins **8** hold the substrate W and the open state in which the holding of the substrate W by the plurality of chuck pins **8** is released. When the substrate W is transferred to the spin chuck **5**, the controller **3** makes the respective chuck pins **8** retract to the open positions. In this state, the controller **3** makes the substrate transfer robot CR operate to place the substrate W on the plurality of chuck pins **8**. Thereafter, the controller **3** makes the respective chuck pins **8** move to the closed positions. The substrate W is thereby held by the plurality of chuck pins **8** in a state where a lower surface of the substrate W and an upper surface of the spin base **7** are separated in an up/down direction. When the controller **3** makes the spin motor **10** rotate in this state, the substrate W rotates around the substrate rotation axis A**1** together with the spin base **7** and the chuck pins **8**.

As shown in FIG. **2**, each processing unit **2** includes a first chemical liquid nozzle **11** that discharges a chemical liquid, such as SPM (a mixed liquid containing H_2SO_4 and H_2O_2), etc., toward an upper surface of the substrate W, a first nozzle arm **12** having a tip portion on which the first chemical liquid nozzle **11** mounted, and a first nozzle moving device **13** that moves the first nozzle arm **12** to move the first chemical liquid nozzle **11**.

As shown in FIG. **2**, the first chemical liquid nozzle **11**, which serves in common as a reaction liquid nozzle, is held in an inwardly facing attitude by the first nozzle arm **12**. The inwardly facing attitude is an attitude in which a processing liquid is discharged in a discharge direction that is inclined with respect to the upper surface of the substrate W so that the processing liquid lands at a position further inward (toward the substrate rotation axis A**1** side) than a processing liquid discharge port. The first chemical liquid nozzle **11** is not restricted to being held in the inwardly facing attitude and may instead be held by the first nozzle arm **12** in a perpendicular attitude in which the processing liquid is discharged in a direction perpendicular to the upper surface of the substrate W or may be held by the first nozzle arm **12** in an outwardly facing attitude in which the processing liquid is discharged in a discharge direction that is inclined with respect to the upper surface of the substrate W so that the processing liquid lands at a position further outward (toward the side opposite to the substrate rotation axis A**1** side) than the processing liquid discharge port.

As shown in FIG. **3**, the first nozzle moving device **13** rotates the first nozzle arm **12** around a first nozzle rotation axis A**2** extending in a vertical direction at a periphery of the spin chuck **5** to make the first chemical liquid nozzle **11** move horizontally along a path passing through an upper surface central portion of the substrate W in a plan view. The first nozzle moving device **13** makes the first chemical liquid nozzle **11** move horizontally between a processing position at which the chemical liquid discharged from the first chemical liquid nozzle **11** lands on the upper surface of the substrate W and a retracted position at which the first chemical liquid nozzle **11** is retracted to the periphery of the spin chuck **5** in a plan view (position shown in FIG. **3**). Further, the first nozzle moving device **13** makes the first chemical liquid nozzle **11** move horizontally among a central position at which the chemical liquid discharged from the first chemical liquid nozzle **11** lands at the upper surface central portion of the substrate W, an intermediate position at which the chemical liquid discharged from the first chemical liquid nozzle **11** lands at an upper surface intermediate portion of the substrate W, and a peripheral edge position at which the chemical liquid discharged from the first chemical liquid nozzle **11** lands at an upper surface peripheral edge portion of the substrate W. The central position, the intermediate position, and the peripheral edge positions are all processing positions.

The upper surface central portion of the substrate W is a circular region that includes the center of the upper surface, and the upper surface peripheral edge portion of the substrate W is an annular region that includes the outer edge of the upper surface. The upper surface intermediate portion of the substrate W is an annular region between the outer edge of the upper surface central portion and the inner edge of the upper surface peripheral edge portion. The widths of the upper surface central portion, the upper surface intermediate portion, and the upper surface peripheral edge portion are, for example, as follows. Width of the central portion (distance in the radial direction from the center of the substrate W to the outer edge of the central portion): $5/15$ of the radius of the substrate W. Width of the intermediate portion (distance in the radial direction from the inner edge of the intermediate portion to the outer edge of the intermediate portion): $9/15$ of the radius of the substrate W. Width of the peripheral edge portion (distance in the radial direction from the inner edge of the peripheral edge portion to the outer edge of the peripheral edge portion): $1/15$ of the radius of the substrate W. These proportions are an example and do not restrict the application of other proportions.

As shown in FIG. **2**, each processing unit **2** includes a first chemical liquid piping **14** that guides the SPM or other chemical liquid to the first chemical liquid nozzle **11**, a stirring piping **15** that stirs the sulfuric acid and the hydrogen peroxide water inside the first chemical liquid piping **14**, and a mixing valve **16** that mixes the sulfuric acid and the hydrogen peroxide water supplied to the first chemical liquid piping **14** at an upstream side of the stirring piping **15**.

As shown in FIG. **2**, each processing unit **2** includes a sulfuric acid tank **17** containing sulfuric acid (liquid), which is an example of a heat generating chemical liquid, a first heater **21** heating the sulfuric acid to maintain the sulfuric acid inside the sulfuric acid tank **17** at a temperature (a fixed temperature in a range of 60 to 90° C., for example, 80° C.) higher than room temperature, a sulfuric acid piping **18** guiding the sulfuric acid inside the sulfuric acid tank **17** to the mixing valve **16**, a sulfuric acid valve **19** opening and closing the interior of the sulfuric acid piping **18**, and a sulfuric acid flow control valve **20** increasing and decreasing the flow rate of the sulfuric acid supplied from the sulfuric acid piping **18** to the mixing valve **16**. Although not illustrated, the sulfuric acid flow control valve **20** includes a valve body having a valve seat provided in the interior, a valve element opening and closing the valve seat, and an actuator that moves the valve element between an open position and a closed position. The same applies to other flow control valves.

As shown in FIG. **2**, each processing unit **2** includes a hydrogen peroxide water tank **22** containing hydrogen peroxide water, which is an example of a reaction chemical liquid, a first hydrogen peroxide water piping **23** guiding the hydrogen peroxide water having room temperature (within a range of 20° C. to 30° C., for example, 25° C.) inside the hydrogen peroxide water tank **22** to the mixing valve **16**, a first hydrogen peroxide water valve **24** opening and closing the interior of the first hydrogen peroxide water piping **23**, and a first hydrogen peroxide water flow control valve **25** increasing and decreasing the flow rate of the hydrogen peroxide water supplied from the first hydrogen peroxide water piping **23** to the mixing valve **16**.

As shown in FIG. **2**, each processing unit **2** further includes a second hydrogen peroxide water piping **26** guiding the hydrogen peroxide water inside the hydrogen peroxide water tank **22** into the first chemical liquid piping **14**, a second hydrogen peroxide water valve **27** opening and closing the interior of the second hydrogen peroxide water piping **26**, and a second hydrogen peroxide water flow control valve **28** increasing and decreasing the flow rate of the hydrogen peroxide water supplied from the second hydrogen peroxide water piping **26** to the first chemical liquid piping **14**. An upstream end of the second hydrogen peroxide water piping **26** is connected to the first hydrogen peroxide water piping **23** at a position further upstream than the first hydrogen peroxide water valve **24** and the first hydrogen peroxide water flow control valve **25**, and a downstream end of the second hydrogen peroxide water piping **26** is connected to the first chemical liquid piping **14** at a position further upstream than the mixing piping **15**.

When the sulfuric acid valve **19** is opened, the high-temperature sulfuric acid is supplied from the sulfuric acid piping **18** to the mixing valve **16** at a flow rate corresponding to the opening degree of the sulfuric acid flow control valve **20**. Also, when the first hydrogen peroxide water valve **24** is opened, the room-temperature hydrogen peroxide water inside the hydrogen peroxide water tank **22** is supplied from the first hydrogen peroxide water piping **23** to the mixing valve **16** at a flow rate corresponding to the opening degree of the first hydrogen peroxide water flow control valve **25**. The sulfuric acid and the hydrogen peroxide water are thereby supplied to the mixing valve **16** at predetermined proportions (if "X1" is the proportion of sulfuric acid and "Y1" is the proportion of hydrogen peroxide water, for example, $X1>Y1$).

The sulfuric acid and the hydrogen peroxide water supplied to the mixing valve **16** are supplied from the first chemical liquid piping **14** to the first chemical liquid nozzle **11** via the mixing piping **15**. In this process, the sulfuric acid and the hydrogen peroxide water are mixed at the mixing valve **16** and stirred at the stirring piping **15**. The sulfuric acid and the hydrogen peroxide water are thereby mixed uniformly, and the mixed liquid (SPM) of the sulfuric acid and the hydrogen peroxide water is heated by the reaction of the sulfuric acid and the hydrogen peroxide water to a first temperature (of not less than 100° C., for example, 160° C.) higher than the temperatures of the sulfuric acid and the hydrogen peroxide water before mixing. The SPM having high temperature (the first temperature) that is formed by the mixing of the sulfuric acid and the hydrogen peroxide water is thus discharged from the first chemical liquid nozzle **11**. SPM is a mixed chemical liquid that contains peroxymonosulfuric acid, which has a high oxidizing power.

Also, when the sulfuric acid valve **19** and the first hydrogen peroxide water valve **24** are closed and the second hydrogen peroxide water valve **27** is opened, the room-temperature hydrogen peroxide water inside the hydrogen peroxide water tank **22** bypasses the mixing valve **16** and flows into the first chemical liquid piping **14** from the second hydrogen peroxide water piping **26**. The room-temperature hydrogen peroxide water is thereby supplied from the second hydrogen peroxide water piping **26** to the first chemical liquid piping **14** at a flow rate corresponding to the opening degree of the second hydrogen peroxide water flow control valve **28**. The room-temperature hydrogen peroxide water supplied to the first chemical liquid piping **14** is discharged from the first chemical liquid nozzle **11**.

As shown in FIG. **2**, each processing unit **2** includes a second chemical liquid nozzle **29** that discharges a chemical liquid, such as SC**1** (a mixed liquid containing NH_4OH and H_2O_2) etc., toward the upper surface of the substrate W, a second nozzle arm **30** having a tip portion on which the second chemical liquid nozzle **29** mounted, and a second nozzle moving device **31** that moves the second nozzle arm **30** to move the second chemical liquid nozzle **29**. FIG. **2** shows an example where the second chemical liquid nozzle **29** is held in an inwardly facing attitude by the second nozzle arm **30**. The second chemical liquid nozzle **29** is not restricted to being held in the inwardly facing attitude and may instead be held by the second nozzle arm **30** in a perpendicular attitude or in an outwardly facing attitude.

As shown in FIG. **3**, the second nozzle moving device **31** rotates the second nozzle arm **30** around a second nozzle rotation axis A**3** extending in the vertical direction at a periphery of the spin chuck **5** to make the second chemical liquid nozzle **29** move horizontally along a path passing through an upper surface central portion of the substrate W in a plan view. The second nozzle moving device **31** makes the second chemical liquid nozzle **29** move horizontally between a processing position at which the chemical liquid discharged from the second chemical liquid nozzle **29** lands on the upper surface of the substrate W and a retracted position at which the second chemical liquid nozzle **29** is retracted to the periphery of the spin chuck **5** in a plan view. Further, the second nozzle moving device **31** makes the second chemical liquid nozzle **29** move horizontally among a central position, an intermediate position, and a peripheral edge position.

As shown in FIG. **2**, each processing unit **2** includes a second chemical liquid piping **33** that guides the SC**1**, having a temperature (for example, 30 to 50° C.) lower than the temperature of the SPM (first temperature) and higher than room temperature, to the second chemical liquid nozzle **29** and a second chemical liquid valve **34** opening and closing the interior of the second chemical liquid piping **33**. When the second chemical liquid valve **34** is opened, the SC**1** from a second chemical liquid supply source is supplied from the second chemical liquid piping **33** to the second chemical liquid nozzle **29**. The SC**1** (liquid) of, for example, 40° C. is thereby discharged from the second chemical liquid nozzle **29**.

As shown in FIG. **2**, each processing unit **2** includes a rinse liquid nozzle **36** discharging a rinse liquid toward the upper surface of the substrate W, a third nozzle arm **37** having a tip portion on which the rinse liquid nozzle **36** mounted, and a third nozzle moving device **38** that moves the third nozzle arm **37** to move the rinse liquid nozzle **36**. FIG. **2** shows an example where the rinse liquid nozzle **36** is held in an inwardly facing attitude by the third nozzle arm **37**. The rinse liquid nozzle **36** is not restricted to being held in the inwardly facing attitude and may instead be held by the third nozzle arm **37** in a perpendicular attitude or in an outwardly facing attitude.

Although not illustrated, the third nozzle moving device **38** rotates the third nozzle arm **37** around a third nozzle rotation axis extending in the vertical direction at a periphery of the spin chuck **5** to make the rinse liquid nozzle **36** move horizontally along a path passing through an upper surface central portion of the substrate W in a plan view. The third nozzle moving device **38** makes the rinse liquid nozzle **36** move horizontally between a processing position at which the rinse liquid discharged from the rinse liquid nozzle **36** lands on the upper surface of the substrate W and a retracted position at which the rinse liquid nozzle **36** is retracted to the periphery of the spin chuck **5** in a plan view. Further, the third nozzle moving device **38** makes the rinse liquid nozzle **36** move horizontally among a central position, an intermediate position, and a peripheral edge position.

As shown in FIG. **2**, each processing unit **2** includes a first rinse liquid piping **39** that guides the rinse liquid from a rinse liquid supply source to the rinse liquid nozzle **36**, a first rinse liquid valve **40** opening and closing the interior of the first rinse liquid piping **39**, and a first rinse liquid flow control valve **41** increasing and decreasing the flow rate of the rinse liquid supplied from the first rinse liquid piping **39** to the rinse liquid nozzle **36**. Each processing unit **2** further includes a second rinse liquid piping **42** that guides the rinse liquid from the rinse liquid supply source to the rinse liquid nozzle **36**, a second rinse liquid valve **43** opening and closing the interior of the second rinse liquid piping **42**, and a second rinse liquid flow control valve **44** increasing and decreasing the flow rate of the rinse liquid supplied from the second rinse liquid piping **42** to the rinse liquid nozzle **36**.

When the first rinse liquid valve **40** is opened, the rinse liquid having room temperature (for example, 25° C.) is discharged from the rinse liquid nozzle **36** at a flow rate corresponding to the opening degree of the first rinse liquid flow control valve **41**. Similarly, when the second rinse liquid valve **43** is opened, the rinse liquid having room temperature (for example, 25° C.) is discharged from the rinse liquid nozzle **36** at a flow rate corresponding to the opening degree of the second rinse liquid flow control valve **44**. The rinse liquid discharged from the rinse liquid nozzle **36** is pure water (deionized water). The rinse liquid supplied to the rinse liquid nozzle **36** is not restricted to pure water and may instead be carbonated water, electrolyzed ion water, hydrogen water, ozone water, IPA (isopropyl alcohol), or aqueous hydrochloric acid solution of dilute concentration (for example, approximately 10 to 100 ppm), etc.

The opening degree of the first rinse liquid flow control valve **41** may be greater or smaller than the opening degree of the second rinse liquid flow control valve **44** or may be equal to the opening degree of the second rinse liquid flow control valve **44**. When the opening degrees of the first rinse liquid flow control valve **41** and the second rinse liquid flow control valve **44** differ, the flow rate of the rinse liquid discharged from the rinse liquid nozzle **36** can be changed by switching between the first rinse liquid valve **40** and the second rinse liquid valve **43** and without changing the opening degrees of the first rinse liquid flow control valve **41** and the second rinse liquid flow control valve **44**.

As shown in FIG. **2**, each processing unit **2** includes a lower surface nozzle **45** discharging a heating liquid toward a lower surface central portion of the substrate W, a heating liquid piping **46** guiding the heating liquid to the lower surface nozzle **45**, a heating liquid valve **47** opening and closing the interior of the heating liquid piping **46**, a heating liquid flow control valve **48** increasing and decreasing the flow rate of the heating liquid supplied from the heating liquid piping **46** to the lower surface nozzle **45**, and a heating liquid heater **49** heating the heating liquid, supplied from the heating liquid piping **46** to the lower surface nozzle **45** at a temperature (for example, of 50 to 90° C.) lower than the temperature (first temperature) of the SPM and higher than room temperature.

When the heating liquid valve **47** is opened, the heating liquid from a heating liquid supply source is supplied from the heating liquid piping **46** to the lower surface nozzle **45** at a flow rate corresponding to the opening degree of the heating liquid flow control valve **48**. The heating liquid having high temperature (for example, 60° C.), which is an example of a heating fluid (heating liquid), is thereby discharged from the lower surface nozzle **45**. As shown in FIG. **2**, the heating liquid supplied from the lower surface nozzle **45** is heated pure water. The type of heating liquid supplied to the lower surface nozzle **45** is not restricted to pure water and may instead be carbonated water, electrolyzed ion water, hydrogen water, ozone water, IPA (isopropyl alcohol), or aqueous hydrochloric acid solution of dilute concentration (for example, approximately 10 to 100 ppm), etc.

As shown in FIG. **2** and FIG. **3**, the lower surface nozzle **45** includes a disk portion **50**, disposed in a horizontal attitude at a height between an upper surface central portion of the spin base **7** and the lower surface central portion of the substrate W, and a cylindrical portion **51** extending downward from the disk portion **50**. The heating liquid from the heating liquid piping **46** is supplied to the interior of the cylindrical portion **51** and is discharged upward from a discharge port **45***a* opening at an upper surface of the disk portion **50**. The disk portion **50** and the cylindrical portion **51** are not contact with a rotating portion, such as the spin shaft **9**, and the lower surface nozzle **45** is fixed at a fixed position. The cylindrical portion **51** is disposed inside the cylindrical spin shaft **9**. An inner peripheral surface of the spin shaft **9** surrounds an outer peripheral surface of the cylindrical portion **51** over the entire periphery and across an interval in the radial direction. As shown in FIG. **2**, the inner peripheral surface of the spin shaft **9** and the outer peripheral surface of the cylindrical portion **51** define a cylindrical gas flow passage **52** that extends along the substrate rotation axis A**1**. An upper end of the gas flow passage **52** that serves as a gas discharge port **53** opens at the upper surface central portion of the spin base **7**.

As shown in FIG. **2**, each processing unit **2** includes a gas piping **54** guiding a gas from a gas supply source to the gas flow passage **54**, a gas valve **55** opening and closing the interior of the gas piping **54**, a gas flow control valve **56** increasing and decreasing the flow rate of the gas supplied from the gas piping **54** to the gas flow passage **52**, and a gas heater **57** heating the gas, supplied from the gas piping **54** to the gas flow passage **52** at a temperature (for example, of 50 to 90° C.) lower than the temperature (first temperature) of the SPM and higher than room temperature.

When the gas valve **55** is opened, the gas from the gas supply source is supplied from the gas piping **54** to the gas flow passage **52** at a flow rate corresponding to the opening degree of the gas flow control valve **56**. The gas supplied to the gas flow passage **52** flows upward inside the gas flow passage **52** and is discharged upward from the gas discharge port **53**. The gas discharged from the gas discharge port **53** spreads radially between the lower surface of the substrate W and the upper surface of the spin base **7**. The space between the lower surface of the substrate W and the upper surface of the spin base **7** is thereby filled with the gas having high temperature (for example, 80° C.), which is an example of a heating fluid (heating gas). The gas discharged from the gas discharge port **53** is nitrogen gas, which is an example of an inert gas. The gas is not restricted to nitrogen gas and may instead be an inert gas other than nitrogen gas or may be another gas, such as water vapor, etc.

As shown in FIG. **2**, the cup **6** is disposed further outward than the substrate W held by the spin chuck **5**. The cup **6** surrounds the spin base **7**. When a processing liquid is supplied to the substrate W in a state where the spin chuck **5** is rotating the substrate W, the processing liquid splashes from the substrate W to a periphery of substrate W. When the processing liquid is supplied to the substrate W, an upper end portion of the upwardly open cup **6** is disposed higher than the spin base **7**. The processing liquid, such as the chemical liquid, the rinse liquid, etc., that is expelled to the periphery of the substrate W is thus received by the cup **6**. The processing liquid received by the cup **6** is guided to an unillustrated recovery device or drain device.

As shown in FIG. **2**, the heating device includes the infrared heater **58** disposed above the substrate W held by the spin chuck **5**, a heater arm **59** having a tip portion on which the infrared heater **58** mounted, and a heater moving device **60** that moves the heater arm **59** to move the infrared heater **58**.

As shown in FIG. **2**, the infrared heater **58** includes an infrared lamp **61** emitting light that includes infrared rays and a lamp housing **62** housing the infrared lamp **61**. The infrared lamp **61** is disposed inside the lamp housing **62**. As shown in FIG. **3**, the lamp housing **62** is smaller than the substrate W in a plan view. The infrared heater **58** is thus smaller than the substrate W in a plan view. The infrared lamp **61** and the lamp housing **62** are mounted on the heater arm **59**. The infrared lamp **61** and the lamp housing **62** thus move together with the heater arm **59**.

As shown in FIG. **4**, the infrared lamp **61** is connected to the controller **3**. The electric power supplied to the infrared lamp **61** is adjusted by the controller **3**. The infrared lamp **61** is, for example, a halogen lamp. Instead of a halogen lamp, the infrared lamp **61** may be another heat generating element, such as a carbon heater, etc. The infrared lamp **61** includes a filament and a quartz tube housing the filament. At least a portion of the lamp housing **62** is made of quartz or other material with light transmitting property and heat resistance. Therefore when the infrared lamp **61** emits light, the light from the infrared lamp **61** is transmitted through the lamp housing **62** and is radiated outward from the outer surface of the lamp housing **62**.

As shown in FIG. **4**, the lamp housing **62** has a bottom wall that is parallel to the upper surface of the substrate W. The infrared lamp **61** is disposed above the bottom wall. A lower surface of the bottom wall includes a substrate facing surface **58***a* that is parallel to the upper surface of the substrate W and is flat. In a state where the infrared heater **58** is disposed above the substrate W, the substrate facing surface **58***a* of the infrared heater **58** faces the upper surface of the substrate W in the up/down direction across an interval. When the infrared lamp **61** emits light in this state, the light including the infrared rays is directed from the substrate facing surface **58***a* toward the upper surface of the substrate W and is irradiated on the upper surface of the substrate W. The substrate facing surface **58***a* has, for example, a circular shape with a diameter smaller than the radius of the substrate W. The substrate facing surface **58***a* is not restricted to having a circular shape and may have a rectangular shape with the length in the longitudinal direction being not less than the radius of the substrate W and less than the diameter of the substrate W or may have a shape other than a circular shape or a rectangular shape.

As shown in FIG. **4**, the infrared lamp **61** includes an annular portion **63** with ends that is disposed along a horizontal plane and a pair of vertical portions **64** extending upward from one end portion and another end portion of the annular portion **63**. The lamp housing **62** includes a transmitting member that allows transmission of infrared rays. The transmitting member includes a cylindrical housing portion **65** that extends in the up/down direction and a disk-shaped bottom plate portion **66** that closes a lower end of the housing portion **65**. The lamp housing **62** further includes a lid member **67** closing an upper end of the housing portion **65** and a supporting member **68** supporting the pair of vertical portions **64** of the infrared lamp **61**. The infrared lamp **61** is supported by the lid member **67** via the supporting member **68**. The annular portion **63** of the infrared lamp **61** is disposed in a space demarcated by the housing portion **65**, the bottom plate portion **66**, and the lid member **67**. The bottom plate portion **66** is disposed below the infrared lamp **61** and faces the infrared lamp **61** in the up/down direction across an interval.

As shown in FIG. **2**, the heater moving device **60** holds the infrared heater **58** at a predetermined height. As shown in FIG. **3**, the heater moving device **60** rotates the heater arm **59** around a heater rotation axis A**4** extending in a vertical direction at a periphery of the spin chuck **5** to move the infrared heater **58** horizontally. The irradiation position onto which the infrared rays are irradiated (a region of a portion within the upper surface of the substrate W) is thereby moved within the upper surface of the substrate W. The heater moving device **60** moves the infrared heater **58** horizontally along a path passing through the center of the substrate W in a plan view. The infrared heater **58** thus moves within a horizontal plane that includes a portion above the spin chuck **5**. Also, the heater moving device **60** moves the infrared heater **58** in the vertical direction to change the distance between the substrate facing surface **58** and the substrate W.

As shown in FIG. **4**, the light from the infrared heater **58** is irradiated onto the irradiation position within the upper surface of the substrate W. In the state where the infrared heater **58** is emitting infrared rays, the controller **3** makes the infrared heater **58** rotate around the heater rotation axis A**4** by the heater moving device **60** while making the substrate W rotate by the spin chuck **5**. The upper surface of the substrate W is thereby scanned by the irradiation position as a heating position. Therefore, when the infrared lamp **61** emits infrared rays in the state where a liquid, such as a processing liquid, etc., is held on the substrate W, the temperatures of the substrate W and the processing liquid rise.

First Processing Example

FIG. **5** is a time chart in outline of a first processing example performed by a processing unit **2**. FIGS. **6**A and **6**B are a specific time chart of a portion of the first processing example. In the following, a resist removing process of removing a resist pattern, which has become unnecessary, from a substrate W shall be described with reference to FIG. **2** and FIG. **5**. FIGS. **6**A and **6**B shall also be referenced as necessary.

When the substrate W is to be processed by the processing unit **2**, a carrying-in step of carrying the substrate W into the chamber **4** is performed (step S**1** of FIG. **5**). Specifically, in a state where all of the nozzles, etc., are retracted from above the spin chuck **5**, the controller **3** makes the hand of the substrate transfer robot CR that holds the substrate W enter inside the chamber **4**. The controller **3** then makes the substrate transfer robot CR place the substrate W on the plurality of chuck pins **8**. Thereafter, the controller **3** makes the hand of the substrate transfer robot CR retract from inside the chamber **4**. Also, after the substrate W has been placed on the plurality of chuck pins **8**, the controller **3** makes the respective chuck pins **8** move from the open positions to the closed positions. Thereafter the controller **3** starts the rotation of the substrate W by the spin motor **10**.

Thereafter, a first chemical liquid supplying step (step S**2** of FIG. **5**) of supplying the SPM having high temperature (first temperature), which is an example of a first chemical liquid, to the substrate W is performed. Specifically, the controller **3** controls the spin motor **10** to accelerate the substrate W to a first chemical liquid rotation speed V**1** (see FIGS. **6**A and **6**B) and makes the substrate W be rotated at the first chemical liquid rotation speed V**1**. That is, the controller **3** maintains the rotation speed of the substrate W at the first chemical liquid rotation speed V**1**. Further, the controller **3** controls the first nozzle moving device **13** to make the first chemical liquid nozzle **11** move from the retracted position to the processing position. The first chemical liquid nozzle **11** is thereby positioned above the substrate W. Thereafter, the controller **3** opens the sulfuric acid valve **19** and the first hydrogen peroxide water valve **24** to make the first chemical liquid nozzle **11** discharge the SPM having the first temperature (for example, 160° C.) toward the upper surface of the substrate W that is rotating at the first chemical liquid rotation speed V**1**. The controller **3** controls the first nozzle moving device **13** to make the liquid landing position of the SPM with respect to the upper surface of the substrate W move between the central portion and the peripheral edge portion in this state.

The SPM discharged from the first chemical liquid nozzle **11** lands on the upper surface of the substrate W and thereafter flows outward along the upper surface of the substrate W due to a centrifugal force. The SPM is thus supplied to the entirety of the upper surface of the substrate W and a liquid film of SPM that covers the entire upper surface of the substrate W is thereby formed on the substrate W. The resist film and the SPM are thereby made to undergo a chemical reaction and the resist film on the substrate W is removed from the substrate W by the SPM. Further, the controller **3** makes the liquid landing position of the SPM with respect to the upper surface of the substrate W move between the central portion and the peripheral edge portion in the state where the substrate W is rotating so that the liquid landing position of the SPM passes through the entire upper surface of the substrate W and the entire upper surface of the substrate W is scanned. The SPM discharged from the first chemical liquid nozzle **11** is thus supplied to the entire upper surface of the substrate W and the entire upper surface of the substrate W is processed uniformly.

Thereafter, a puddle step of holding the liquid film of SPM on the substrate W in a state where the discharge of SPM is stopped (step S**3** of FIG. **5**) is performed. Specifically, the controller **3** controls the spin motor **10** to decelerate the substrate W to a second chemical liquid rotation speed V**2**, lower than the rotation speed of the substrate W in the first chemical liquid supplying step (first chemical liquid rotation speed V**1**), in the state where the entire upper surface of the substrate W is covered by the liquid film of SPM (see FIGS. **6**A and **6**B) and makes the substrate W rotate at the second chemical liquid rotation speed V**2**. The centrifugal force applied to the SPM on the substrate W thus weakens and the flow rate of SPM expelled from the substrate W decreases. In the state where the substrate W is rotating at the second chemical liquid rotation speed V**2**, the controller **3** closes the sulfuric acid valve **19** and the first hydrogen peroxide water valve **24** to stop the discharge of SPM from the first chemical liquid nozzle **11**. The liquid film of SPM that covers the entire upper surface of the substrate W is thereby held on the substrate W in the state where the discharge of SPM is stopped. After stopping the discharge of SPM, the controller **3** controls the first nozzle moving device **13** to put the first chemical liquid nozzle **11** on standby above the substrate W.

Also, a heating step (step S**4** of FIG. **5**) of using the infrared heater **58** to heat the substrate W and the SPM on the substrate W at a heating temperature, which is higher than the temperature (first temperature) of the SPM before the SPM is supplied to the substrate W, is performed in parallel to the first chemical liquid supplying step (step S**2** of FIG. **5**) and the puddle step (step S**3** of FIG. **5**). Specifically, the controller **3** controls the heater moving device **60** to move the infrared heater **58** from the retracted position to the processing position. The infrared heater **58** is thereby positioned above the substrate W. Thereafter, the controller **3** makes the infrared heater **58** start emitting light. The temperature of the infrared heater **58** thus rises to the heating temperature (for example, of not less than 200° C.) that is not less than the boiling point of the SPM at its current concentration and is maintained at the heating temperature.

After the infrared heater **58** starts emitting light at a position above the substrate W, the controller **3** makes the infrared heater **58** move by the heater moving device **60** to make the position of irradiation of the infrared rays with respect to the upper surface of the substrate W move within the upper surface of the substrate W. After the heating of the substrate W by the infrared heater **58** has been performed for a predetermined time, the controller **3** makes the infrared heater **58** stop emitting light in the state where the substrate W is rotating at the second chemical liquid rotation speed V**2** and the liquid film of SPM covering the entire upper surface of the substrate W is held on the substrate W. Thereafter, the controller **3** controls the heater moving device **60** to retract the infrared heater **58** from above the substrate W. The emitting of light and moving of the infrared heater **58** may be performed simultaneously or the moving may be started after the emitting of light.

The controller **3** thus makes the position of irradiation of the infrared rays with respect to the upper surface of the substrate W move within the upper surface of the substrate W in the state where the substrate W is being rotated and therefore the substrate W is heated uniformly. The liquid film of SPM covering the entire upper surface of the substrate W is thus also heated uniformly. The temperature of heating of the substrate W by the infrared heater **58** is set to a temperature not less than the boiling point of the SPM at its current concentration. The SPM on the substrate W is thus heated to the boiling point at its current concentration. In particular, when the temperature of heating of the substrate W by the infrared heater **58** is set to a temperature higher than the boiling point of the SPM at its current concentration, the temperature at the interface of the substrate W and the SPM is maintained at a temperature higher than the boiling point to promote removal of foreign matter (resist film) from the substrate W.

Thereafter, a reaction liquid supplying step (step S**5** of FIG. **5**) of supplying hydrogen peroxide water, which is an example of a reaction liquid causing an exothermic reaction upon mixing with sulfuric acid and having a temperature before being supplied to the substrate W of less than the temperature (first temperature) of the SPM and not less than the temperature (second temperature) of a rinse liquid supplied to the substrate W in a first rinse liquid supplying step (step S**7** of FIG. **5**) to be described below, to the substrate W and a first temperature decrease suppressing step (step S**6** of FIG. **5**) of supplying pure water, which is an example of a heating fluid having a first intermediate temperature, lower than the temperature (first temperature) of the SPM and higher than the temperature (second temperature) of the rinse liquid, as the temperature before being supplied to the substrate W, to the lower surface of the substrate W are performed in parallel.

In regard to the reaction liquid supplying step, the controller **3** controls the first nozzle moving device **13** to position the first chemical liquid nozzle **11** at the intermediate position at which the processing liquid discharged from the first chemical liquid nozzle **11** lands on the upper surface intermediate portion of the substrate W. Thereafter, the controller **3** opens the second hydrogen peroxide water valve **27** to make the hydrogen peroxide water having room temperature be discharged from the first chemical liquid nozzle **11** toward the upper surface of the substrate W that is rotating at the second chemical liquid rotation speed V**2**. The supplying of the hydrogen peroxide water of a lower temperature than the substrate W and the SPM is thereby started at the upper surface intermediate portion of the substrate W.

As shown in FIGS. **6**A and **6**B, after the supplying of the hydrogen peroxide water is started at the upper surface intermediate portion of the substrate W, the controller **3** controls the first nozzle moving device **13** to move the first chemical liquid nozzle **11** from the intermediate position to the central position in the state where the substrate W is rotating at the second chemical liquid rotation speed V**2**. The liquid landing position of the hydrogen peroxide water is thereby moved from the upper surface intermediate portion of the substrate W to the upper surface central portion. Thereafter, the controller **3** closes the second hydrogen peroxide water valve **27** to stop the discharge of hydrogen peroxide water from the first chemical liquid nozzle **11**. In succession, the controller **3** controls the first nozzle moving device **13** to make the first chemical liquid nozzle **11** retract from above the substrate W.

In regard to the first temperature decrease suppressing step, the controller **3** makes pure water of the first intermediate temperature (for example, a temperature higher than room temperature) be discharged from the lower surface nozzle **45** toward the lower surface of the substrate W that is rotating at the second chemical liquid rotation speed V**2**. The pure water discharged from the lower surface nozzle **45** lands on the lower surface central portion of the substrate W and thereafter flows outward along the lower surface of the substrate W to the peripheral edge of the substrate W due to a centrifugal force. The pure water is thereby supplied to the entire lower surface of the substrate W. Temperature decrease of the substrate W and the SPM is thus suppressed. After elapse of a predetermined time from the opening of the heating liquid valve **47**, the controller **3** closes the heating liquid valve **47** to stop the discharge of pure water from the lower surface nozzle **45**. Thereafter, the controller **3** opens and closes the gas valve **55** to make nitrogen gas be discharged temporarily from the gas discharge port **53**. The pure water is thereby expelled from between the substrate W and the spin base **7**.

In the reaction liquid supplying step, the hydrogen peroxide water of a lower temperature than the SPM supplied to the substrate W is discharged from the first chemical liquid nozzle **11** toward the upper surface central portion of the substrate W. The hydrogen peroxide water that lands on the upper surface central portion of the substrate W spreads along the substrate W from the liquid landing position to a periphery of the liquid landing position. Further, the hydrogen peroxide water on the substrate W flows outward along the substrate W toward the peripheral edge of the substrate W while flowing along the substrate W in a circumferential direction toward the downstream side of the rotation direction. The hydrogen peroxide water is thereby supplied to the entire upper surface of the substrate W covered by the liquid film of SPM. The hydrogen peroxide water discharged from the first chemical liquid nozzle **11** thus flows along the substrate W while taking away the heat of the substrate W and the SPM that are higher in temperature than the hydrogen peroxide water.

A portion of the SPM on the substrate W is expelled from the peripheral edge of the substrate W to the periphery thereof due to the supplying of the hydrogen peroxide water and is received by the cup **6**. Also, the remaining SPM on the substrate W is diluted by the hydrogen peroxide water and gradually decreases in concentration. The entire upper surface of the substrate W is thus covered by the liquid film that contains the SPM and the hydrogen peroxide water and the proportion of the hydrogen peroxide water in the liquid film gradually increases. The sulfuric acid concentration in the SPM thus gradually decreases.

The temperatures of the substrate W and the SPM (especially the temperatures at the liquid landing position and the vicinity thereof) decrease because the hydrogen peroxide water, which is lower in temperature than the substrate W and the SPM, is supplied to the substrate W, to the substrate W. However, the sulfuric acid contained in the SPM generates heat due to reaction with the hydrogen peroxide water and therefore significant decrease of the temperatures of the substrate W and the SPM at the liquid landing position is suppressed or prevented. Further, the temperature decrease amounts of the substrate W and the SPM at the liquid landing position are reduced by the first temperature decrease suppressing step being performed in parallel to the reaction liquid supplying step. Increase of the temperature difference of the substrate W between the liquid landing position and other positions can thus be suppressed. Deformation of the substrate W due to the temperature difference can thus be suppressed and the amount of warping of the substrate W can be reduced.

In the reaction liquid supplying step, the temperatures of the substrate W and the SPM decrease gradually due to the supplying of the hydrogen peroxide water as the reaction liquid. The temperature difference of the hydrogen peroxide water with respect to the substrate W and the SPM is thus greatest when the supplying of the hydrogen peroxide water is started. The supplying of the hydrogen peroxide water is started at the upper surface intermediate portion of the substrate W at which the circumferential speed is greater than that at the upper surface central portion of the substrate W. Therefore, the supply flow rate of the hydrogen peroxide water per unit area is lower than in a case where the supplying of the hydrogen peroxide water is started at the upper surface central portion of the substrate W. The temperatures of the substrate W and the SPM at the liquid landing position can thus be suppressed or prevented from decreasing suddenly and rapidly due to the supplying of a large amount of the hydrogen peroxide water. Further, the hydrogen peroxide water that lands on the upper surface central portion of the substrate W is expelled to the periphery of the substrate W via the upper surface peripheral edge portion of the substrate W and therefore the retention time of the hydrogen peroxide water on the substrate W is longer than in a case where the supplying of the hydrogen peroxide water is started at the upper surface peripheral edge portion of the substrate W. The hydrogen peroxide water can thus be used efficiently.

Also as shown in FIG. **2**, the first chemical liquid nozzle **11** discharges the hydrogen peroxide water inwardly. Therefore the hydrogen peroxide water discharged from the first chemical liquid nozzle **11** mainly flows inwardly from the liquid landing position along the substrate W. The hydrogen peroxide water can thus be spread to a region further inward than the liquid landing position in a shorter time than in a case where the first chemical liquid nozzle **11** discharges the hydrogen peroxide water in the direction perpendicular to the upper surface of the substrate W or in a case where the first chemical liquid nozzle **11** discharges the hydrogen peroxide water outwardly. Further, the flow rate of the hydrogen peroxide water flowing inwardly from the liquid landing position is increased in comparison to these cases and the retention time of the hydrogen peroxide water on the substrate W is thus increased. The hydrogen peroxide water can thus be used efficiently.

Thereafter, the first rinse liquid supplying step (step S**7** of FIG. **5**) of supplying pure water having room temperature, which is an example of the rinse liquid having the second temperature, to the substrate W is performed. Specifically, the controller **3** controls the third nozzle moving device **38** to move the rinse liquid nozzle **36** from the retracted position to the processing position. Thereafter, the controller **3** opens the first rinse liquid valve **40** to make the pure water having room temperature be discharged from the rinse liquid nozzle **36** toward the upper surface central portion of the substrate W. Further, the controller **3** controls the spin motor **10** to accelerate the substrate W to a rinse rotation speed V**3** greater than the first chemical liquid rotation speed V**1** and the second chemical liquid rotation speed V**2** (see FIGS. **6**A and **6**B) and makes the substrate W rotate at the rinse rotation speed V**3**. When a predetermined time has elapsed from the opening of the first rinse liquid valve **40**, the controller **3** closes the first rinse liquid valve **40** to stop the discharge of pure water from the rinse liquid nozzle **36**. Thereafter, the controller **3** controls the third nozzle moving device **38** to make the rinse liquid nozzle **36** retract from above the substrate W.

The pure water discharged from the rinse liquid nozzle **36** lands on the upper surface central portion of the substrate W that is covered by the chemical liquid or the reaction liquid. The chemical liquid on the substrate W is thus forced to flow away from the central portion to a periphery thereof. The pure water that has landed on the upper surface central portion of the substrate W flows outward along the upper surface of the substrate W due to a centrifugal force. Similarly, the chemical liquid on the substrate W flows outward along the upper surface of the substrate W due to the centrifugal force. Further, the substrate W is rotating at the rinse rotation speed V**3** greater than the first chemical liquid rotation speed V**1** and the second chemical liquid rotation speed V**2** and therefore a greater centrifugal force is applied to the liquid on the substrate W than those applied in the first chemical liquid supplying step and the reaction liquid supplying step. The liquid film of pure water thus spreads instantly from the central portion of the substrate W to the peripheral edge of the substrate W and the chemical liquid on the substrate W is replaced by the pure water in a short time. The chemical liquid on the substrate W is thereby rinsed off by the pure water.

Thereafter, a second chemical liquid supplying step (step S**8** of FIG. **5**) of supplying the SC**1**, which is an example of a second chemical liquid having a temperature before being supplied to the substrate W of less than the temperature (first temperature) of the SPM and higher than the temperature (second temperature) of the rinse liquid, to the substrate W, and a second temperature decrease suppressing step (step S**9** of FIG. **5**) of supplying pure water, which is an example of a heating fluid having a second intermediate temperature, lower than the temperature (first temperature) of the SPM and higher than the temperature (second temperature) of the rinse liquid, as the temperature before being supplied to the substrate W, to the lower surface of the substrate W are performed in parallel.

In regard to the second chemical liquid supplying step, the controller **3** controls the second nozzle moving device **31** to move the second chemical liquid nozzle **29** from the retracted position to the processing position. After the second chemical liquid nozzle **29** has been positioned above the substrate W, the controller **3** opens the second chemical liquid valve **34** to make the SC**1** be discharged from the second chemical liquid nozzle **29** toward the upper surface of the substrate W that is in the rotating state. In this state, the controller **3** controls the second nozzle moving device **31** to make the liquid landing position of the SC**1** with respect to the upper surface of the substrate W move between the central portion and the peripheral edge portion. When a predetermined time elapses from the opening of the second chemical liquid valve **34**, the controller **3** closes the second chemical liquid valve **34** to stop the discharge of the SC**1**. Thereafter, the controller **3** controls the second nozzle moving device **31** to make the second chemical liquid nozzle **29** retract from above the substrate W.

The SC**1** discharged from the second chemical liquid nozzle **29** lands on the upper surface of the substrate W and thereafter flows outward along the upper surface of the substrate W due to the centrifugal force. The pure water on the substrate W is thus forced to flow outward by the SC**1** and is expelled to a periphery of the substrate W. The liquid film of pure water on the substrate W is thereby replaced by the liquid film of SC**1** that covers the entire upper surface of the substrate W. Further, the controller **3** makes the liquid landing position of the SC**1** with respect to the upper surface of the substrate W move between the central portion and the peripheral edge portion in the state where the substrate W is rotating so that the liquid landing position of the SC**1** passes through the entire upper surface of the substrate W and the entire upper surface of the substrate W is scanned. The SC**1** discharged from the second chemical liquid nozzle **29** is thus supplied to the entire upper surface of the substrate W and the entire upper surface of the substrate W is processed uniformly.

In regard to the second temperature decrease suppressing step, the controller **3** makes pure water of the second intermediate temperature be discharged from the lower surface nozzle **45** toward the lower surface of the rotating substrate W. The pure water having high temperature is thereby supplied to the entire lower surface of the substrate W. The temperature of the substrate W, which has been decreased to the second temperature by the supplying of the rinse liquid having the second temperature, can thereby be prevented from changing locally due to the supplying of the SC**1** having the temperature higher than the second temperature. After elapse of a predetermined time from the opening of the heating liquid valve **47**, the controller **3** closes the heating liquid valve **47** to stop the discharge of pure water from the lower surface nozzle **45**. Thereafter, the controller **3** opens and closes the gas valve **55** to make nitrogen gas be discharged temporarily from the gas discharge port **53**. The pure water is thereby expelled from between the substrate W and the spin base **7**.

Thereafter, a second rinse liquid supplying step (step S**10** of FIG. **5**) of supplying pure water having room temperature, which is an example of the rinse liquid, to the substrate W is performed. Specifically, the controller **3** controls the third nozzle moving device **38** to move the rinse liquid nozzle **36** from the retracted position to the processing position. After the rinse liquid nozzle **36** has been positioned above the substrate W, the controller **3** opens the first rinse liquid valve **40** to make the pure water be discharged from the rinse liquid nozzle **36** toward the upper surface of the substrate W that is in the rotating state. The SC**1** on the substrate W is thereby forced to flow outward by the pure water and is expelled to the periphery of the substrate W. The liquid film of SC**1** on the substrate W is thus replaced by the liquid film of pure water that covers the entire upper surface of the substrate W. When a predetermined time elapses from the opening of the first rinse liquid valve **40**, the controller **3** closes the first rinse liquid valve **40** to stop the discharge of pure water. Thereafter the controller **3** controls the first nozzle moving device **13** to make the rinse liquid nozzle **36** retract from above the substrate W.

Thereafter a drying step (step S**11** of FIG. **5**) of drying the substrate W is performed. Specifically, the controller **3** controls the spin motor **10** to accelerate the substrate W to a drying rotation speed (for example of several thousand rpm) greater than the rotation speeds in the first chemical liquid supplying step (step S**2** of FIG. **5**) to the second rinse liquid supplying step (step S**10** of FIG. **5**) and makes the substrate W rotate at the drying rotation speed. A large centrifugal force is thereby applied to the liquid on the substrate W and the liquid attached to the substrate W is spun off to the periphery of the substrate W. The substrate W is thereby removed of liquid and the substrate W dries. After a predetermined time elapses from the start of high-speed rotation of the substrate W, the controller **3** controls the spin motor **10** to stop the rotation of the substrate W by the spin chuck **5**.

Thereafter, a carrying-out step (step S**12** of FIG. **5**) of carrying out the substrate W from inside the chamber **4** is performed. Specifically, the controller **3** moves the respective chuck pins **8** from the closed positions to the open positions to release the clamping of the substrate W by the spin chuck **5**. Thereafter in the state where all nozzles, etc., are retracted from above the spin chuck **5**, the controller **3** makes the hand of the substrate transfer robot CR enter inside the chamber **4**. The controller **3** then makes the hand of the substrate transfer robot CR hold the substrate W on the spin chuck **5**. Thereafter, the controller **3** makes the hand of the substrate transfer robot CR retract from inside the chamber **4**. The processed substrate W is thereby carried out of the chamber **4**.

Although a case where the hydrogen peroxide water having room temperature, which is an example of the reaction liquid, is supplied to the upper surface of the substrate W in the reaction liquid supplying step was described in the above description of the first processing example, pure water having room temperature, which is an example of the reaction liquid, may be supplied instead of the hydrogen peroxide water to the upper surface of the substrate W covered by the SPM. Specifically, in place of the reaction liquid supplying step (step S**5**) of supplying the hydrogen peroxide water having room temperature to the substrate W, a reaction liquid supplying step (step S**5***a*) of supplying the pure water having room temperature to the substrate W may be executed in parallel to the first temperature decrease suppressing step (step S**6** of FIG. **5**) as shown in FIGS. **6**A and **6**B.

In this case, the controller **3** controls the third nozzle moving device **38** to position the rinse liquid nozzle **36** at the intermediate position at which the rinse liquid discharged from the rinse liquid nozzle **36** lands on the upper surface intermediate portion of the substrate W. Thereafter, the controller **3** opens the second rinse liquid valve **43** to make pure water having room temperature, which has a temperature lower than the temperature (first temperature) of the SPM and causes an exothermic reaction upon mixing with sulfuric acid, be discharged from the rinse liquid nozzle **36** toward the upper surface of the substrate W that is rotating at the second chemical liquid rotation speed V**2** and is covered by the liquid film of SPM. The supplying of the pure water having lower temperature than the substrate W and the SPM is thereby started at the upper surface intermediate portion of the substrate W.

As shown in FIGS. **6**A and **6**B, after the supplying of the pure water is started at the upper surface intermediate portion of the substrate W, the controller **3** controls the third nozzle moving device **38** to make the rinse liquid nozzle **36** move from the intermediate position to the central position in the state where the substrate W is rotating at the second chemical liquid rotation speed V**2**. The liquid landing position of the pure water is thereby moved from the upper surface intermediate portion of the substrate W to the upper surface central portion. Further, similarly to the case where the hydrogen peroxide water is supplied, the SPM on the substrate W is diluted by the pure water while generating heat due to the supplying of the pure water. After a predetermined time elapses from the opening of the second rinse liquid valve **43**, the controller **3** closes the second rinse liquid valve **43** to stop the discharge of the pure water from the rinse liquid nozzle **36** in the state where the rinse liquid nozzle **36** is positioned at the central position. Thereafter, the controller **3** starts the first rinse liquid supplying step (step S**7** of FIG. **5**). That is, the controller **3** makes the substrate W rotate at the rinse rotation speed V**3** in the state where the first rinse liquid valve **40** is open.

Second Processing Example

FIGS. **7**A and **7**B are a specific time chart of a portion of a second processing example performed by the processing unit **2**. FIG. **2** and FIGS. **7**A and **7**B shall be referenced in the following description.

The second processing example differs from the first processing example in that in the reaction liquid supplying step, the liquid landing position of the reaction liquid with respect to the upper surface of the substrate W is moved from the peripheral edge portion to the central portion. In other words, the steps besides the reaction liquid supplying step are the same as those of the first processing example. The reaction liquid supplying step in the case where the reaction liquid is hydrogen peroxide water (step S**5** of FIGS. **7**A and **7**B) and the reaction liquid supplying step in the case where the reaction liquid is pure water (step S**5***a* of FIGS. **7**A and **7**B) shall thus be described below.

In the case where the reaction liquid is hydrogen peroxide water, the controller **3** controls the first nozzle moving device **13** to position the first chemical liquid nozzle **11** at the peripheral edge position at which the processing liquid discharged from the first chemical liquid nozzle **11** lands on the upper surface peripheral edge portion of the substrate W. Thereafter, the controller **3** opens the second hydrogen peroxide water valve **27** to make the hydrogen peroxide water having room temperature be discharged from the first chemical liquid nozzle **11** toward the upper surface of the substrate W that is rotating at the second chemical liquid rotation speed V**2**. The supplying of the hydrogen peroxide water of a lower temperature than the substrate W and the SPM is thereby started at the upper surface peripheral edge portion of the substrate W.

After the supplying of the hydrogen peroxide water is started at the upper surface peripheral edge portion of the substrate W, the controller **3** controls the first nozzle moving device **13** to move the first chemical liquid nozzle **11** from the peripheral edge position to the central position in the state where the substrate W is rotating at the second chemical liquid rotation speed V**2**. The liquid landing position of the hydrogen peroxide water is thereby moved from the upper surface peripheral edge portion of the substrate W to the upper surface central portion. Thereafter, the controller **3** closes the second hydrogen peroxide water valve **27** to stop the discharge of hydrogen peroxide water from the first chemical liquid nozzle **11**. In succession, the controller **3** controls the first nozzle moving device **13** to make the first chemical liquid nozzle **11** retract from above the substrate W.

On the other hand, in the case where the reaction liquid is pure water, the controller **3** controls the third nozzle moving device **38** to position the rinse liquid nozzle **36** at the peripheral edge position at which the rinse liquid discharged from the rinse liquid nozzle **36** lands on the upper surface peripheral edge portion of the substrate W. Thereafter, the controller **3** opens the second rinse liquid valve **43** to make pure water having room temperature be discharged from the rinse liquid nozzle **36** toward the upper surface of the substrate W that is rotating at the second chemical liquid rotation speed V**2**. The supplying of the pure water having lower temperature than the substrate W and the SPM is thereby started at the upper surface peripheral edge portion of the substrate W.

After the supplying of the pure water is started at the upper surface peripheral edge portion of the substrate W, the controller **3** controls the third nozzle moving device **38** to make the rinse liquid nozzle **36** move from the peripheral edge position to the central position in the state where the substrate W is rotating at the second chemical liquid rotation speed V**2**. The liquid landing position of the pure water is thereby moved from the upper surface peripheral edge portion of the substrate W to the upper surface central portion. Therefore, similarly to the case where the hydrogen peroxide water is supplied, the SPM on the substrate W is diluted by the pure water while generating heat due to the supplying of the pure water. The controller **3** then closes the second rinse liquid valve **43** to stop the discharge of the pure water from the rinse liquid nozzle **36** in the state where the rinse liquid nozzle **36** is positioned at the central position. Thereafter, the controller **3** starts the first rinse liquid supplying step (step S**7** of FIG. **5**).

In the second processing example, the supplying of the reaction liquid is thus started at the upper surface peripheral edge portion of the substrate W and the temperature thus decreases gradually from the peripheral edge portion of the substrate W. The deformation of the peripheral edge portion of the substrate W, to which the clamping force of the chuck pin **8** is applied, can thus be prevented before the central portion and the intermediate portion of the substrate W. Deflection of the rotating substrate W can thereby be suppressed or prevented. Further, by moving the liquid landing position of the reaction liquid with respect to the upper surface of the substrate W toward the central portion of the substrate W, the reaction liquid can be spread across the entire upper surface of the substrate W in a short time. The deformation amount of the substrate W can thus be reduced while suppressing localized temperature decrease of the substrate W by the exothermic reaction of the SPM and the reaction liquid.

Third Processing Example

FIG. **8** is a specific time chart of a portion of a third processing example performed by the processing unit **2**. FIG. **2** and FIG. **8** shall be referenced in the following description.

The third processing example differs from the first processing example in that the rotation speed of the substrate W in the reaction liquid supplying step is a third chemical liquid rotation speed V**4** that is greater than the rotation speed V**2** of the substrate W in the puddle step and less than the rotation speed V**3** of the substrate W in the first rinse liquid supplying step. In other words, the steps besides the reaction liquid supplying step are the same as those of the first processing example. The reaction liquid supplying step in the case where the reaction liquid is hydrogen peroxide water (step S**5** of FIG. **8**) and the reaction liquid supplying step in the case where the reaction liquid is pure water (step S**5***a* of FIG. **8**) shall thus be described below.

In the case where the reaction liquid is hydrogen peroxide water, the controller **3** controls the first nozzle moving device **13** to position the first chemical liquid nozzle **11** at the intermediate position or the peripheral edge position. Thereafter, the controller **3** opens the second hydrogen peroxide water valve **27** to make the hydrogen peroxide water having room temperature be discharged from the first chemical liquid nozzle **11** toward the upper surface of the substrate W that is rotating at the second chemical liquid rotation speed V**2**. The supplying of the hydrogen peroxide water of a lower temperature than the substrate W and the SPM is thereby started at the upper surface intermediate portion or the upper surface peripheral edge portion of the substrate W.

After the supplying of the hydrogen peroxide water is started or at the same time that the supplying is started, the controller **3** controls the spin motor **10** to accelerate the substrate W to the third chemical liquid rotation speed V**4** greater than the second chemical liquid rotation speed V**2** and makes the substrate W rotate at the third chemical liquid rotation speed V**4**. Thereafter, the controller **3** controls the first nozzle moving device **13** to move the first chemical liquid nozzle **11** from the intermediate position or the peripheral edge position to the central position in the state where the substrate W is rotating at the third chemical liquid rotation speed V**4**. The liquid landing position of the hydrogen peroxide water is thereby moved from the upper surface intermediate portion or the upper surface peripheral edge portion of the substrate W to the upper surface central portion. Thereafter, the controller **3** closes the second hydrogen peroxide water valve **27** to stop the discharge of hydrogen peroxide water from the first chemical liquid nozzle **11**. In succession, the controller **3** controls the first nozzle moving device **13** to make the first chemical liquid nozzle **11** retract from above the substrate W.

On the other hand, in the case where the reaction liquid is pure water, the controller **3** controls the third nozzle moving device **38** to position the rinse liquid nozzle **36** at the intermediate position or the peripheral edge position. Thereafter, the controller **3** opens the second rinse liquid valve **43** to make pure water having room temperature be discharged from the rinse liquid nozzle **36** toward the upper surface of the substrate W that is rotating at the second chemical liquid rotation speed V**2**. The supplying of the pure water having lower temperature than the substrate W and the SPM is thereby started at the upper surface intermediate portion or the upper surface peripheral edge portion of the substrate W.

After the supplying of the pure water is started or at the same time that the supplying is started, the controller **3** controls the spin motor **10** to accelerate the substrate W to the third chemical liquid rotation speed V**4** a greater than the second chemical liquid rotation speed V**2** and makes the substrate W rotate at the third chemical liquid rotation speed V**4**a. Thereafter, the controller **3** controls the third nozzle moving device **38** to make the rinse liquid nozzle **36** move from the intermediate position or the peripheral edge position to the central position in the state where the substrate W is rotating at the third chemical liquid rotation speed V**4**a. The liquid landing position of the pure water is thereby moved from the upper surface peripheral edge portion of the substrate W to the upper surface central portion. Therefore, similarly to the case where the hydrogen peroxide water is supplied, the SPM on the substrate W is diluted by the pure water while generating heat due to the supplying of the pure water. The controller **3** then closes the second rinse liquid valve **43** to stop the discharge of the pure water from the rinse liquid nozzle **36** in the state where the rinse liquid nozzle **36** is positioned at the central position. Thereafter, the controller **3** starts the first rinse liquid supplying step (step S**7** of FIG. **5**).

FIG. **8** shows an example where, regardless of whether the reaction liquid is hydrogen peroxide water or pure water, the rotation speed (the third chemical liquid rotation speed V**4** or V**4**a) of the substrate W is fixed during the discharge of the reaction liquid. However, the third chemical liquid rotation speed V**4** or V**4**a does not have to be fixed.

Also, FIG. **8** shows an example where the third chemical liquid rotation speed V**4** a for the case where the reaction liquid is pure water is less than the third chemical liquid rotation speed V**4** for the case where the reaction liquid is hydrogen peroxide water. This is because if conditions besides the type of reaction liquid are the same, the heat generation amount of the SPM is lower when the reaction liquid is pure water than when the reaction liquid is hydrogen peroxide water. By making the third chemical liquid rotation speed V**4** a for the case where the reaction liquid is pure water less than the third chemical liquid rotation speed V**4** for the case where the reaction liquid is hydrogen peroxide water to increase the retention time of pure water on the substrate W, the heat generation amount of SPM is increased to enable sudden temperature change of the substrate W and the SPM to be suppressed favorably.

However, the present invention is not restricted to the above and the third chemical liquid rotation speed V**4** a for the case where the reaction liquid is pure water may be made equal to or may be made greater than the third chemical liquid rotation speed V**4** for the case where the reaction liquid is hydrogen peroxide water.

Fourth Processing Example

FIG. **9** is a specific time chart of a portion of a fourth processing example performed by the processing unit **2**. FIG. **2** and FIG. **9** shall be referenced in the following description.

The fourth processing example differs from the first processing example in that in step S**13** of FIG. **9**, the reaction liquid is supplied to the substrate W while using the infrared heater **58** to heat the substrate W at a temperature lower than the heating temperature of the substrate W in the first chemical liquid supplying step (step S**2** of FIG. **9**) and the puddle step (step S**3** of FIG. **9**). In other words, besides a post-heating step (step S**13** of FIG. **9**), in which the infrared heater **58** is used to heat the substrate W at a post-heating temperature lower than the heating temperature of the substrate W in the heating step (step S**4** of FIG. **9**), being performed in parallel to the reaction liquid supplying step (step S**5** of FIG. **9**), the process is the same as that of the first processing example. The point of difference with respect to the first processing example shall thus mainly be described below.

After performing the heating step (step S**4** of FIG. **9**) of heating the substrate W and the SPM on the substrate W at the predetermined heating temperature by the infrared heater **58** disposed above the substrate W, the post-heating step (step S**13** of FIG. **9**), in which the infrared heater **58** is used to heat the substrate W and the liquid (a liquid including at least one among SPM, hydrogen peroxide water, and pure water) on the substrate W at the post-heating temperature lower than the heating temperature of the substrate W in the heating step, is performed in parallel to the reaction liquid supplying step (step S**5** of FIG. **9**).

Specifically, after the infrared heater **58** has heated the substrate W at the heating temperature in the heating step, the controller **3** decreases the electric power supplied to the infrared heater **58** to a second electric power, lower than the electric power (first electric power) in the heating step, with the hydrogen peroxide water being discharged as the reaction liquid toward the upper surface of the substrate W and the infrared heater **58** being positioned above the substrate W. The second electric power has a value less than the first electric power and not less than zero. Therefore, while making the infrared heater **58** emit light or while stopping the light emission by the infrared heater **58**, the controller **3** heats the substrate W and the liquid on the substrate W at the post-heating temperature by the heat energy emitted from the infrared heater **58** or by the residual heat of the infrared heater **58**. FIG. **9** illustrates a case where the second electric power has a value greater than zero and the light emission by the infrared heater **58** is being continued.

After the heating of the substrate W and the liquid on the substrate W at the post-heating temperature by the infrared heater **58** has been performed for a predetermined time, the controller **3** controls the heater moving device **60** to make the infrared heater **58** retract from above the substrate W in the state where the light emission by the infrared heater **58** is stopped. While the substrate W and the liquid on the substrate W are being heated at the post-heating temperature by the infrared heater **58**, the controller **3** may move the position of heating by the infrared heater **58** by moving the infrared heater **58** above the substrate W by the heater moving device **60** or may keep the infrared heater **58** stationary above the substrate W. Also, the controller **3** may decrease the electric power supplied to the infrared heater **58** from the first electric power to the second electric power continuously or in steps. The controller **3** may stop the supply of electric power to the infrared heater **58** to heat the substrate W and the liquid on the substrate W by the residual heat of the infrared heater **58**.

Also the electric power (second electric power) supplied to the infrared heater **58** in the post-heating step may include an initial electric power less than the electric power (first electric power) supplied to the infrared heater **58** in the heating step and greater than zero and a terminal electric power less than the initial electric power and not less than zero. That is, the electric power supplied to the infrared heater **58** may be decreased continuously or in steps from the initial electric power to the terminal electric power and the heat energy transmitted to the substrate W and the liquid on the substrate W in the post-heating step may be decreased with the elapse of time. In this case, the temperatures of the substrate W and the liquid on the substrate W can be decreased gradually while preventing localized temperature change in the substrate W.

As described above, with the present preferred embodiment, the chemical liquid having the first temperature (the SPM having high temperature) is supplied to the upper surface of the substrate W. The reaction liquid (the hydrogen peroxide water or the pure water having room temperature) is then supplied to the upper surface of the substrate W in the state where the chemical liquid remains on the substrate W. The reaction liquid supplied to the substrate W mixes with the chemical liquid remaining on the substrate W. The proportion of the reaction liquid in the liquid remaining on the substrate W (the liquid containing the chemical liquid and the reaction liquid) thus increases and the concentration of the chemical liquid decreases. The rinse liquid having the second temperature (the pure water having room temperature) lower than the first temperature is supplied to the upper surface of the substrate W after the reaction liquid has been supplied to the substrate W. The liquid remaining on the substrate W is thereby rinsed off.

When the supplying of the reaction liquid is started, the temperature of the substrate W approaches the temperature of the reaction liquid. The temperature of the reaction liquid before being supplied to the substrate W is lower than the temperature (first temperature) of the chemical liquid and not less than the temperature (second temperature) of the rinse liquid. Upon mixing with the chemical liquid, the reaction liquid causes an exothermic reaction in the chemical liquid. Therefore, when the reaction liquid is supplied to the upper surface of the substrate W in the state where the chemical liquid remains on the substrate W, the exothermic reaction occurs at the liquid landing position of the reaction liquid and at positions in the vicinity of the liquid landing position so that the temperature decrease amount of the substrate W is reduced in the liquid landing position vicinity region. The temperature of the substrate W thus approaches the temperature of the reaction liquid gradually. Sudden and rapid temperature decrease of the substrate W can thus be suppressed to reduce the amount of deformation of the substrate W in comparison to a case where the rinse liquid is supplied to the substrate in succession to the supplying of the chemical liquid.

Further, in parallel to the supplying of the reaction liquid to the upper surface of the substrate W, the high-temperature heating fluid (the high-temperature pure water or nitrogen gas) is supplied to the lower surface of the substrate W. The temperature of the heating fluid before being supplied to the substrate W is lower than the temperature (first temperature) of the chemical liquid and higher than the liquid temperature of the reaction liquid before being supplied to the substrate W. Localized temperature decrease of the substrate W due to the supplying of the reaction liquid is thus suppressed by the heating fluid being supplied to the substrate W in parallel to the supplying of the reaction liquid. Further, the temperature decrease of the substrate W can be suppressed without hindering the reaction of the chemical liquid and the substrate W because the heating fluid is supplied to the lower surface of the substrate W at the opposite side of the surface to which the chemical liquid and the reaction liquid are supplied.

Also in the present preferred embodiment, the supplying of the reaction liquid to the upper surface of the substrate W is started at the intermediate portion, between the central portion and the peripheral edge portion, in the state where the substrate W is rotating and the entire upper surface is covered by the chemical liquid. In succession, the liquid landing position of the reaction liquid with respect to the upper surface of the substrate W is moved from the intermediate portion to the central portion. The centrifugal force due to the rotation of the substrate W is applied to the reaction liquid and the reaction liquid supplied to the substrate W thus flows outward to the peripheral edge portion along the upper surface of the substrate W. The reaction liquid is thereby supplied to the entire upper surface of the substrate W. The proportion of the reaction liquid in the liquid film covering the entire upper surface of the substrate W thus increases gradually and the temperatures of the respective portions of the substrate W approach the temperature of the reaction liquid.

The temperature difference between the substrate W and the reaction liquid is greatest when the supplying of the reaction liquid is started. The circumferential speed (speed in the rotation direction) at the upper surface intermediate portion of the substrate W is greater than the circumferential speed at the upper surface central portion of the substrate W, and therefore, the supply flow rate of the reaction liquid per unit area is lower than in a case where the supplying of the reaction liquid is started at the upper surface central portion of the substrate W. The temperatures of the substrate W and the chemical liquid at the liquid landing position can thus be suppressed or prevented from decreasing suddenly and rapidly due to the supplying of a large amount of the reaction liquid. Further, the reaction liquid that lands on the upper surface central portion of the substrate W is expelled to the periphery of the substrate W via the upper surface peripheral edge portion of the substrate W and therefore the retention time of the reaction liquid on the substrate W is longer than in a case where the supplying of the reaction liquid is started at the upper surface peripheral edge portion of the substrate W. The reaction liquid can thus be used efficiently.

Also with the present preferred embodiment, the reaction liquid is discharged toward the upper surface of the substrate W in the direction that is inclined with respect to the upper surface of the substrate W. The reaction liquid is thus discharged obliquely with respect to the upper surface of the substrate W. The impact when the reaction liquid lands on the substrate W is thus smaller than in a case where the reaction liquid is made perpendicularly incident on the upper surface of the substrate W. In a case where a pattern is formed on the upper surface of the substrate W, if the impact applied to the substrate W is reduced, the impact applied to the pattern is reduced. Occurrence of damage, such as pattern collapse, etc., can thus be suppressed or prevented.

Also with the present preferred embodiment, the reaction liquid is discharged toward the upper surface of the substrate W in the direction that is inclined with respect to the upper surface of the substrate W so as to be positioned closer to the center of the substrate W as the direction approaches the upper surface of the substrate W. The reaction liquid thus mainly flows inwardly (toward the center of the substrate W) from the liquid landing position along the substrate W. The reaction liquid can thus be spread to a region further inward than the liquid landing position in a shorter time than in a case where the reaction liquid is discharged in the direction perpendicular to the upper surface of the substrate W or in a case where the reaction liquid is discharged in a direction that is inclined outwardly with respect to the upper surface of the substrate W. Further, the flow rate of the reaction liquid flowing inwardly from the liquid landing position is increased in comparison to these cases and the retention time of the reaction liquid on the substrate W is thus increased. The reaction liquid can thus be used efficiently.

Also with the present preferred embodiment, a reaction chemical liquid (hydrogen peroxide water) of a liquid temperature lower than the first temperature and not less than the second temperature is mixed with a heat generating chemical liquid (sulfuric acid) that generates heat upon mixing with the reaction chemical liquid. The heat generating chemical liquid and the reaction chemical liquid are thus raised in temperature to the first temperature by the heat generation of the heat generating chemical liquid to form the chemical liquid (SPM) of the first temperature. The reaction chemical liquid as the reaction liquid is supplied to the upper surface of the substrate W in the state where the chemical liquid remains on the substrate W. The reaction chemical liquid as the reaction liquid thus mixes with the heat generating chemical liquid contained in the chemical liquid on the substrate W and an exothermic reaction occurs at the liquid landing position of the reaction liquid and at positions in its vicinity. The temperature decrease amount of the substrate W in the liquid landing position vicinity region is thus decreased. Further, a chemical liquid of the same type as a component chemical liquid (the reaction chemical liquid in the present case) contained in the chemical liquid, that is, a liquid with a high affinity to the chemical liquid is used as the reaction liquid and therefore the chemical liquid and the reaction liquid can be mixed efficiently.

Also with the third processing example, the reaction liquid is discharged toward the upper surface of the substrate W in a state where the substrate W is rotating at the relatively high rotation speed V**4**, that is, the rotation speed V**4** that is higher than the rotation speed V**2** of the substrate W in at least a portion of a period between the start of supplying of the chemical liquid to the substrate W and the start of supplying of the reaction liquid to the substrate W. The centrifugal force applied to the liquid attached to the substrate W thus increases. The chemical liquid remaining on the substrate W is thus spun off rapidly to the periphery of the substrate W and the reaction liquid supplied to the substrate W is spread across the entire upper surface of the substrate W rapidly. The temperature of the entire upper surface of the substrate W thus decreases uniformly so that the deformation of the substrate W due to temperature difference can be suppressed or prevented.

Also with the present preferred embodiment, the supplying of the heating fluid (the pure water having high temperature) to the substrate W is started after the discharge of the chemical liquid (SPM) to the substrate W is stopped. When the chemical liquid is being discharged toward the substrate W, the chemical liquid supplied before is expelled to the periphery of the substrate W. Therefore, when the heating fluid is discharged toward the substrate W in parallel to the discharge of the chemical liquid, a large amount of the chemical liquid may be mixed with the heating fluid at positions around the substrate W. Specifically, a large amount of the SPM may mix with the pure water at the periphery of the substrate W. The chemical liquid expelled from the substrate W may thus rise significantly in temperature and the cup **6** may rise significantly in temperature accordingly.

On the other hand, when the discharge of the chemical liquid is stopped, the chemical liquid expelled from the substrate W is small or zero in amount and therefore a large amount of the chemical liquid will not be mixed with the heating fluid at the periphery of the substrate W. Therefore a large amount of the SPM will not be mixed with the pure water at the periphery of the substrate W. Therefore, even in a case where the chemical liquid generates heat due to mixing with the heating fluid (for example, in a case where the chemical liquid is a liquid that contains sulfuric acid and the heating fluid is a gas or liquid that contains water), the chemical liquid expelled from the substrate W can be prevented from rising significantly in temperature. Temperature rise of the cup **6** or other cylindrical capturing member that captures the liquid expelled from the substrate W can thus be suppressed.

Second Preferred Embodiment

A second preferred embodiment of the present invention shall now be described. In FIG. **10** to FIG. **14** below, component portions equivalent to respective portions indicated in FIG. **1** to FIG. **9** described above are provided with the same reference symbols as in FIG. **1**, etc., and description thereof shall be omitted.

FIG. **10** is a plan view of the spin chuck **5** according to the second preferred embodiment of the present invention. FIG. **11** is a front view of the spin chuck **5** according to the second preferred embodiment of the present invention. FIG. **12** is a schematic plan view of a lower surface nozzle **245**. FIG. **13** is a schematic sectional view of the internal arrangement of the lower surface nozzle **245**.

As shown in FIG. **10** and FIG. **11**, the processing unit **2** has, in addition to the lower surface nozzle **45** related to the first preferred embodiment, a lower surface nozzle **245** that is changeable in distance from the substrate rotation axis A**1** to the liquid landing position of a processing liquid. As shown in FIG. **11** and FIG. **12**, the lower surface nozzle **245** has a telescopic arm **271** capable of being extended and contracted along the lower surface of the substrate W and a telescopic piping **272** disposed in the interior of the telescopic arm **271**.

As shown in FIG. **13**, the telescopic arm **271** includes a plurality of hollow arm portions (a first arm portion **273** and a second arm portion **274**) disposed above the spin base **7**, a first joint portion **275** coupling a base portion of the first arm portion **273** and a tip portion of the second arm portion **274** so as to be relatively rotatable around a vertical flexure axis A**5**, and a second joint portion **276** supporting the base portion of the second arm portion **274** so as to be rotatable around the substrate rotation axis A**1** with respect to the spin base **7**. The telescopic arm **271** further includes a first spring **277**, urging the first arm portion **273** and the second arm portion **274** around the flexure axis A**5** at an urging force in accordance with the relative rotation amounts of the first arm portion **273** and the second arm portion **274** around the flexure axis A**5**, and a second spring **278**, urging the second arm portion **274** and the spin base **7** around the substrate rotation axis A**1** at an urging force in accordance with the relative rotation amounts of the second arm portion **274** and the spin base **7** around the substrate rotation axis A**1**.

As shown in FIG. **13**, the first joint portion **275** includes a first sleeve **279** extending in the up/down direction along the flexure axis A**5** and a first bearing **280** supporting the first sleeve **279** so as to be rotatable around the flexure axis A**5**. The first sleeve **279** is fixed to the tip portion of the second arm portion **274** and extends upward from the second arm portion **274** to the interior of the first arm portion **273**. The first bearing **280** is disposed in the interior of the first arm portion **273** and is held by the first arm portion **273**. The first spring **277** is wound around the first sleeve **279**. One end portion of the first spring **277** is mounted on the first sleeve **279** and another end portion of the first spring **277** is mounted on the first arm portion **273**. The first spring **277** is capable of extending and contracting elastically around the flexure axis A**5**. When the first joint portion **275** is extended from a flexed position (position shown in FIG. **12**), the first arm portion **273** and the second arm portion **274** are pulled toward the flexed position by the urging force of the first spring **277** that is in accordance with the displacement amount of the first joint portion **275**.

As shown in FIG. **13**, the second joint portion **276** includes a second sleeve **281** extending in the up/down direction along the substrate rotation axis A**1** and a second bearing **282** supporting the second sleeve **281** so as to be rotatable around the substrate rotation axis A**1**. The second sleeve **281** is fixed to the chamber **4** so as not to be rotatable around the substrate rotation axis A**1** and extends upward from the interior of the spin base **7** to the interior of the second arm portion **274** along the substrate rotation axis A**1**. The second bearing **282** is disposed in the interior of the second arm portion **274** and is held by the second arm portion **274**. The second spring **278** is wound around the second sleeve **281**. One end portion of the second spring **278** is mounted on the second sleeve **281** and another end portion of the second spring **278** is mounted on the second arm portion **274**. The second spring **278** is capable of extending and contracting elastically around the substrate rotation axis A**1**. When the second joint portion **276** is rotated clockwise from a flexed position (position shown in FIG. **12**), the second arm portion **274** and the spin base **7** are pulled toward the flexed position by the urging force of the second spring **278** that is in accordance with the displacement amount of the second joint portion **276**.

As shown in FIG. **13**, the telescopic piping **272** passes through the interior of the second sleeve **281** and enters into the interior of the second arm portion **274** and further passes through the interior of the first sleeve **279** and enters into the interior of the first arm portion **273**. An upper end portion of the telescopic piping **272** is fixed to a tip portion of the first arm portion **273**. A fluid discharge port **283**, discharging a processing liquid or a processing gas toward the lower surface of the substrate W, is provided at the tip portion of the first arm portion **273**. The telescopic piping **272** is connected to the heating liquid piping **46** or the gas piping **54**. FIG. **11** shows an example where the telescopic piping **272** is connected to the heating liquid piping **46**. Therefore when the heating liquid valve **47** is opened, the rinse liquid (example of a heating fluid) heated to a temperature higher than room temperature by the heating liquid heater **49** is supplied from the heating liquid piping **46** to the telescopic piping **272** at a flow rate corresponding to the opening degree of the heating liquid flow control valve **48** and is discharged upward toward the lower surface of the substrate W from the fluid discharge port **283**.

The supply flow rate of the processing liquid supplied from the heating liquid piping **46** to the telescopic piping **272** is increased or decreased by the controller **3** changing the opening degree of the heating liquid flow control valve **48**. When the supply flow rate of the processing liquid into the telescopic piping **272** is zero or small, the telescopic piping **272** is contracted in a state of being flexed along the telescopic arm **271** as shown in FIG. **13**. When the supply flow rate of the processing liquid into the telescopic piping **272** increases, a force (liquid pressure) that brings the telescopic piping **272** closer to a rectilinear state of extending rectilinearly is generated in the interior of the telescopic piping **272** and the telescopic piping **272** extends toward the rectilinear state. Also, when in a state where the telescopic piping **272** is extended (a state other than the flexed state), the supply flow rate of the processing liquid into the telescopic piping **272** is reduced, the liquid pressure inside the telescopic piping **272** decreases and the telescopic piping **272** thus contracts toward the flexed state due to the restorative force of the telescopic piping **272**. The telescopic piping **272** thus extends and contracts in accordance with the supply flow rate of the processing liquid.

As indicated by solid lines in FIG. **10**, when the supply flow rate of the processing liquid into the telescopic piping **272** is zero or small, the telescopic arm **271** is maintained, by the first spring **277** and the second spring **278**, in a flexed state, in which the processing liquid discharged upward from the fluid discharge port **283** lands on the lower surface central portion of the substrate W. When the supply flow rate of the processing liquid into the telescopic piping **272** increases, the telescopic piping **272** tends to approach the rectilinear state and therefore a force of approaching an extended state, in which the processing liquid discharged upward from the fluid discharge port **283** lands on a lower surface peripheral edge portion of the substrate W, is applied from the telescopic piping **272** to the telescopic arm **271**. Therefore as indicated by alternate long and two short dashes lines in FIG. **10**, at least one of either of the first joint portion **275** and the second joint portion **276** of the telescopic arm **271** rotates against at least one of either of the first spring **277** and the second spring **278** so that the fluid discharge port **283** moves outward. Also, when the supplying of the processing liquid into the telescopic piping **272** is stopped, the telescopic arm **271** is returned to the flexed state by the restorative force of the first spring **277** and the second spring **278** and the fluid discharge port **283** moves inward.

The liquid landing position of the processing liquid with respect to the lower surface of the substrate W moves in the radial direction of the substrate W in accordance with the distance from the substrate rotation axis **A1** to the fluid discharge port **283**. The relationship between the supply flow rate of the processing liquid into the telescopic piping **272** and the distance from the substrate rotation axis **A1** to the fluid discharge port **283** is adjusted, for example, by the spring constants of the first spring **277** and the second spring **278**. As shown in FIG. **10**, the spring constants of the first spring **277** and the second spring **278** are set so that the fluid discharge port **283** moves horizontally along the radius of the substrate W. The liquid landing position of the processing liquid with respect to the lower surface of the substrate W thus moves rectilinearly along the radius of the substrate W. The spring constant of the first spring **277** is, for example, less than the spring constant of the second spring **278**. The first joint portion **275** is thus extended by a smaller force than the second joint portion **276**. The fluid discharge port **283** thus moves in the radial direction of the substrate W in accordance with the supply flow rate of the processing liquid even when the supply flow rate is low. Further, as the supply flow rate of the processing liquid increases, the liquid landing position of the processing liquid with respect to the lower surface of the substrate W moves outward to enable the difference in supply flow rate of processing liquid per unit area to be reduced.

Fifth Processing Example

FIG. **14** is a specific time chart of a portion of a fifth processing example performed by the processing unit **2**. FIG. **10**, FIG. **11**, and FIG. **14** shall be referenced in the following description.

The fifth processing example differs from the first processing example in that in the first temperature decrease suppressing step (step S**6** of FIG. **14**), the liquid landing position of the heating liquid with respect to the lower surface of the substrate W is moved in the radial direction of the substrate W. In other words, the steps besides the first temperature decrease suppressing step are the same as those of the first processing example. The point of difference with respect to the first processing example shall thus mainly be described below. Also, although in the following description, the first temperature decrease suppressing step performed in parallel to the first chemical liquid supplying step shall mainly be described, the same control as that performed for the first temperature decrease suppressing step may be performed for the second temperature decrease suppressing step performed in parallel to the second chemical liquid supplying step.

In the first temperature decrease suppressing step (step S**6** of FIG. **14**), the controller **3** makes the pure water, which is an example of the heating fluid (heating liquid), be discharged from the lower surface nozzle **245** toward the lower surface of the substrate W that is rotating at the second chemical liquid rotation speed V**2**. Temperature decrease of the substrate W and the SPM is thereby suppressed.

In the reaction liquid supplying step (step S**5** of FIG. **14**), the controller **3** controls the first nozzle moving device **13** to move the liquid landing position of the hydrogen peroxide water (an example of the reaction liquid) with respect to the upper surface of the substrate W from the intermediate portion to the central portion in the state where the substrate W is rotating at the second chemical liquid rotation speed V**2** as shown in FIG. **14**. In the first temperature decrease suppressing step (step S**6** of FIG. **14**), the controller **3** changes the opening degree of the heating liquid flow control valve **48**, that is, changes the extension/contraction amount of the telescopic arm **271** to move the liquid landing position of the pure water (an example of the heating liquid) with respect to the lower surface of the substrate W from the intermediate portion to the central portion so as to be in synchronization with the movement of the liquid landing position of the hydrogen peroxide water from the upper surface intermediate portion to the upper surface central portion of the substrate W as shown in FIG. **14**. The controller **3** then closes the second hydrogen peroxide water valve **27** and the heating liquid valve **47** to stop the discharges of hydrogen peroxide water and the pure water from the first chemical liquid nozzle **11** and the lower surface nozzle **245**. Thereafter, the controller **3** opens and closes the gas valve **55** to make nitrogen gas be discharged temporarily from the gas discharge port **53**. The pure water is thereby expelled from between the substrate W and the spin base **7**.

The controller **3** thus controls the first nozzle moving device **13** and the heating liquid flow control valve **48** so that the distance from the substrate rotation axis A**1** to the liquid landing position of the pure water is equal to the distance from the substrate rotation axis A**1** to the liquid landing position of the hydrogen peroxide water. As long as the distances from the substrate rotation axis A**1** are equal, the liquid landing position of the hydrogen peroxide water and the liquid landing position of the pure water may be positions that are separated in the circumferential direction of the substrate W. In the present processing example, the liquid landing position of the hydrogen peroxide water and the liquid landing position of the pure water are positions at mutually opposite sides of the substrate W. The temperature decrease of the substrate W at the liquid landing position of the hydrogen peroxide water can thus be reduced further than in a case where the liquid landing position of the pure water is fixed at the lower surface central portion of the substrate W. Further, localized temperature decrease of the substrate W can be suppressed without having to form a liquid film of the pure water that covers the entire lower surface of the substrate W and the consumption amount of pure water can thus be reduced.

As described above, with the present preferred embodiment, in parallel to moving the liquid landing position of the reaction liquid with respect to the upper surface of the substrate W, the controller **3** moves the landing position of the heating fluid with respect to the lower surface of the substrate W so that the difference between the distance from the center of the substrate W to the liquid landing position of the reaction liquid and the distance from the center of the substrate W to the landing position of the heating fluid is reduced. The heating fluid is thereby blown onto a position close to the liquid landing position of the reaction liquid. Specifically, the heating fluid is blown onto a position at the opposite side of the liquid landing position of the reaction liquid. The heat of the heating fluid is thus transmitted to the substrate W from the position at the opposite side of the liquid landing position of the reaction liquid and the temperature decrease amount at the liquid landing position of the reaction liquid and positions in the vicinity thereof is reduced further. Deformation of the substrate W due to temperature difference can thereby be suppressed or prevented.

Third Preferred Embodiment

A third preferred embodiment of the present invention shall now be described. In FIG. **15** and FIGS. **16**A and **16**B below, component portions equivalent to respective portions indicated in FIG. **1** to FIG. **14** described above are provided with the same reference symbols as in FIG. **1**, etc., and description thereof shall be omitted.

FIG. **15** is a horizontally-viewed schematic view of the interior of a chamber **4** included in a substrate processing apparatus **1** according to the third preferred embodiment of the present invention.

In addition to the arrangement according to the first preferred embodiment, the processing unit **2** further includes a central nozzle **311**A having a central discharge port **311***a* discharging the reaction liquid toward the upper surface central portion of the substrate W, an intermediate nozzle **311**B having an intermediate discharge port **311***b* discharging the reaction liquid toward the upper surface intermediate portion of the substrate W, and a peripheral edge nozzle **311**C having a peripheral edge discharge port **311***c* discharging the reaction liquid toward the upper surface peripheral edge portion of the substrate W. The central nozzle **311**A, the intermediate nozzle **311**B, and the peripheral edge nozzle **311**C are all examples of the reaction liquid nozzle that discharges the reaction liquid toward the substrate W.

The processing unit **2** further includes a central piping **384** guiding the reaction liquid to the central discharge port **311***a*, a central flow control valve **385** increasing and decreasing the flow rate of the reaction liquid supplied from the central piping **384** to the central discharge port **311***a*, an intermediate piping **386** guiding the reaction liquid to the intermediate discharge port **311***b*, an intermediate flow control valve **387** increasing and decreasing the flow rate of the reaction liquid supplied from the intermediate piping **386** to the intermediate discharge port **311***b*, a peripheral edge piping **388** guiding the reaction liquid to the peripheral edge discharge port **311***c*, and a peripheral edge flow control valve **389** increasing and decreasing the flow rate of the reaction liquid supplied from the peripheral edge piping **388** to the peripheral edge discharge port **311***c*. The processing unit **2** further includes a hydrogen peroxide water piping **390** supplying the hydrogen peroxide water having room temperature to each of the central piping **384**, the intermediate piping **386**, and the peripheral edge piping **388**, a hydrogen peroxide water valve **391** opening and closing the interior of the hydrogen peroxide water piping **390**, a pure water piping **392** supplying the pure water having room temperature to each of the central piping **384**, the intermediate piping **386**, and the peripheral edge piping **388**, and a pure water valve **393** opening and closing the interior of the pure water piping **392**.

The processing unit **2** further includes a fourth nozzle arm **394** holding the central nozzle **311**A, the intermediate nozzle **311**B, and the peripheral edge nozzle **311**C, and a fourth nozzle moving device **395** moving the fourth nozzle arm **394** to move the central nozzle **311**A, the intermediate nozzle **311**B, and the peripheral edge nozzle **311**C horizontally. The fourth nozzle moving device **395** moves the central nozzle **311**A, the intermediate nozzle **311**B, and the peripheral edge nozzle **311**C horizontally between processing positions, at which the reaction liquid discharged from the central discharge port **311***a*, the intermediate discharge port **311***b*, and the peripheral edge discharge port **311***c* lands at the upper surface central portion, the upper surface intermediate portion, and the upper surface peripheral edge portion, respectively, of the substrate W, and retracted positions at which the central nozzle **311**A, the intermediate nozzle **311**B, and the peripheral edge nozzle **311**C are retracted to a periphery of the spin chuck **5** in a plan view.

The central nozzle **311**A, the intermediate nozzle **311**B, and the peripheral edge nozzle **311**C are all held by the fourth nozzle arm **394** in inwardly facing attitudes. One or more of the central nozzle **311**A, the intermediate nozzle **311**B, and the peripheral edge nozzle **311**C may be held in a perpendicular attitude or an outwardly facing attitude. When the central nozzle **311**A, the intermediate nozzle **311**B, and the peripheral edge nozzle **311**C are positioned at the processing positions, the central discharge port **311***a*, the intermediate discharge port **311***b*, and the peripheral edge discharge port **311***c* are positioned at three positions that respectively differ in rectilinear distance from the substrate rotation axis A**1**. The central discharge port **311***a*, the intermediate discharge port **311***b*, and the peripheral edge discharge port **311***c* are disposed at an equal height. One or more of the central discharge port **311***a*, the intermediate discharge port **311***b*, and the peripheral edge discharge port **311***c* may be disposed at a different height.

Sixth Processing Example

FIGS. **16**A and **16**B are a specific time chart of a portion of a sixth processing example performed by the processing unit **2**. FIG. **15** and FIGS. **16**A and **16**B shall be referenced in the following description.

The sixth processing example differs from the first processing example in that in the reaction liquid supplying step, the reaction liquid is discharged toward a plurality of positions within the upper surface of the substrate W in a state where a plurality of reaction liquid nozzles are stationary. In other words, the steps besides the reaction liquid supplying step are the same as those of the first processing example. The reaction liquid supplying step in the case where the reaction liquid is hydrogen peroxide water (step S**5** of FIGS. **16**A and **16**B) and the reaction liquid supplying step in the case where the reaction liquid is pure water (step S**5***a* of FIGS. **16**A and **16**B) shall thus be described below.

In the reaction liquid supplying step, the controller **3** controls the fourth nozzle moving device **395** to move the central nozzle **311**A, the intermediate nozzle **311**B, and the peripheral edge nozzle **311**C from the retracted positions to the processing positions in a state where the first chemical liquid nozzle **11** is retracted from above the substrate W. Thereafter, the controller **3** opens one of either of the hydrogen peroxide water valve **391** and the pure water valve **393** to make the central nozzle **311**A, the intermediate nozzle **311**B, and the peripheral edge nozzle **311**C discharge the hydrogen peroxide water or the pure water as the reaction liquid toward the upper surface of the substrate W that is rotating at the second chemical liquid rotation speed V**2**. The supplying of the reaction liquid having lower temperature than the substrate W and the SPM is thereby started at the upper surface central portion, the upper surface intermediate portion, and the upper surface peripheral edge portion of the substrate W.

The discharge flow rates of the reaction liquid from the central nozzle **311**A, the intermediate nozzle **311**B, and the peripheral edge nozzle **311**C in the reaction liquid supplying step may be equal or different. For example, the opening degrees of the central flow control valve **385**, the intermediate flow control valve **387**, and the peripheral edge flow control valve **389** may be adjusted by the controller **3** so that the discharge flow rate increases in the order of the central nozzle **311**A, the intermediate nozzle **311**B, and the peripheral edge nozzle **311**C. In this case, the supply flow rate of the processing liquid with respect to the upper surface of the substrate W increases in the order of the central portion, the intermediate portion, and the peripheral edge portion to enable the difference in supply flow rate of the processing liquid per unit area to be reduced. Localized temperature decrease of the substrate W can thereby be suppressed.

The controller **3** continues the supplying of the reaction liquid to the upper surface of the substrate W for a predetermined time with the central nozzle **311**A, the intermediate nozzle **311**B, and the peripheral edge nozzle **311**C being made stationary above the substrate W. Thereafter, the controller **3** closes the open valve among the hydrogen peroxide water valve **391** and the pure water valve **393** to stop the discharge of the reaction liquid from the central nozzle **311**A, the intermediate nozzle **311**B, and the peripheral edge nozzle **311**C. The controller **3** then starts the first rinse liquid supplying step (step S**7** of FIG. **5**). The central nozzle **311**A, the intermediate nozzle **311**B, and the peripheral edge nozzle **311**C are connected to a pure water supply source and therefore the controller **3** may perform the first rinse liquid supplying step using the central nozzle **311**A, the intermediate nozzle **311**B, and the peripheral edge nozzle **311**C instead of performing the first rinse liquid supplying step using the rinse liquid nozzle **36**.

As described above, with the present preferred embodiment, in the state where the substrate W is rotating, the reaction liquid is discharged simultaneously toward a plurality of positions within the upper surface of the substrate W that respectively differ in distance from the center of the substrate W. More specifically, the reaction liquid is discharged simultaneously toward the upper surface central portion, the upper surface intermediate portion, and the upper surface peripheral edge portion of the substrate W. Therefore, when the substrate W rotates by one turn or more, the reaction liquid is spread across the entire upper surface of the substrate W. The reaction liquid is thus spread across the entire upper surface of the substrate W in a short time and the temperature of the entire upper surface of the substrate W decreases uniformly. Deformation of the substrate W due to temperature difference can thereby be suppressed or prevented.

Although with FIG. **15**, an example where the processing unit **2** is provided with a plurality of reaction liquid nozzles (the central nozzle **311**A, the intermediate nozzle **311**B, and the peripheral edge nozzle **311**C) was described, the processing unit **2** may instead have a single reaction liquid nozzle that discharges the reaction liquid simultaneously toward a plurality of positions within the upper surface of the substrate W that respectively differ in distance from the center of the substrate W. In this case, the processing unit **2** may include a reaction liquid nozzle **311**X having a slit-shaped discharge port **311***x* extending in the radial direction from the upper surface central portion of the substrate W to the upper surface peripheral edge portion of the substrate W in a plan view as shown in FIG. **17**. Or, the processing unit **2** may include a reaction liquid nozzle **311**Y having a plurality of discharge ports **311***y* aligned in the radial direction of the substrate W from the upper surface central portion of the substrate W to the upper surface peripheral edge portion of the substrate W in a plan view as shown in FIG. **18**.

With each of the arrangements shown in FIG. **17** and FIG. **18**, the reaction liquid is discharged simultaneously toward the entirety of a region that is within the upper surface of the substrate W and includes the radius of the substrate W and lands simultaneously on the entire region in the state where the substrate W is rotating. That is, the reaction liquid is supplied simultaneously to the entire region that is continuous in the radial direction of the substrate W from the center of the substrate W to the peripheral edge of the substrate W. Therefore when the substrate W rotates by one turn or more, the reaction liquid is spread across the entire upper surface of the substrate W. The reaction liquid is thus spread across the entire upper surface of the substrate W in a short time and the temperature of the entire upper surface of the substrate W decreases uniformly. Deformation of the substrate W due to temperature difference can thereby be suppressed or prevented.

Fourth Preferred Embodiment

A fourth preferred embodiment of the present invention shall now be described. In FIG. **19** to FIG. **21** below, component portions equivalent to respective portions indicated in FIG. **1** to FIG. **18** described above are provided with the same reference symbols as in FIG. **1**, etc., and description thereof shall be omitted.

As shown in FIG. **19**, the processing unit **2** includes a pure water piping **426** guiding pure water from a pure water supply source to the interior of the first chemical liquid piping **14**, a pure water valve **427** opening and closing the interior of the pure water piping **426**, and a pure water flow control valve **428** increasing and decreasing the flow rate of the pure water supplied from the pure water piping **426** to the first chemical liquid piping **14**. A downstream end of the pure water piping **426** is connected to the first chemical liquid piping **14** at a position further upstream than the stirring piping **15**.

When the sulfuric acid valve **19** and the hydrogen peroxide water valve **24** are closed and the pure water valve **427** is open, the pure water having room temperature from the pure water supply source flows from the pure water piping **426** into the first chemical liquid piping **14** while bypassing the mixing valve **16**. The pure water having room temperature is thus supplied from the pure water piping **426** to the first chemical liquid piping **14** at a flow rate corresponding to the opening degree of the pure water flow control valve **428**. Therefore, when the sulfuric acid valve **19**, the hydrogen peroxide water valve **24**, and the pure water valve **427** are open, a mixed liquid of SPM and pure water that are mixed at a mixing ratio corresponding to the opening degrees of three flow control valves (the sulfuric acid flow control valve **20**, the hydrogen peroxide water flow control valve **25**, and the pure water flow control valve **428**) is discharged from the first chemical liquid nozzle **11**.

Seventh Processing Example

FIG. **20** is a time chart in outline of a seventh processing example performed by a processing unit **2**. FIG. **21** is a specific time chart of a portion of the seventh processing example. In the following, a resist removing process of removing a resist pattern, which has become unnecessary, from a substrate W shall be described with reference to FIG. **19** and FIG. **20**. FIG. **21** shall also be referenced as necessary.

When the substrate W is to be processed by the processing unit **2**, a carrying-in step of carrying the substrate W into the chamber **4** is performed (step S**1** of FIG. **20**). Specifically, in a state where all of the nozzles, etc., are retracted from above the spin chuck **5**, the controller **3** makes the hand of the substrate transfer robot CR that holds the substrate W enter inside the chamber **4**. The controller **3** then makes the substrate transfer robot CR place the substrate W on the plurality of chuck pins **8**. Thereafter, the controller **3** makes the hand of the substrate transfer robot CR retract from inside the chamber **4**. Also, after the substrate W has been placed on the plurality of chuck pins **8**, the controller **3** makes the respective chuck pins **8** move from the open positions to the closed positions. Thereafter the controller **3** starts the rotation of the substrate W by the spin motor **10**.

Thereafter, a first chemical liquid supplying step (step S2 of FIG. **20**) of supplying the SPM having high temperature (first temperature), which is an example of a first chemical liquid, to the substrate W is performed. Specifically, the controller **3** controls the spin motor **10** to accelerate the substrate W to a first chemical liquid rotation speed V**1** (see FIG. **21**) and makes the substrate W be rotated at the first chemical liquid rotation speed V**1**. That is, the controller **3** maintains the rotation speed of the substrate W at the first chemical liquid rotation speed V**1**. Further, the controller **3** controls the first nozzle moving device **13** to make the first chemical liquid nozzle **11** move from the retracted position to the processing position. The first chemical liquid nozzle **11** is thereby positioned above the substrate W. Thereafter, the controller **3** opens the sulfuric acid valve **19** and the first hydrogen peroxide water valve **24** to make the first chemical liquid nozzle **11** discharge the SPM having the first temperature (for example, 160° C.) toward the upper surface of the substrate W that is rotating at the first chemical liquid rotation speed V**1**. The controller **3** controls the first nozzle moving device **13** to make the liquid landing position of the SPM with respect to the upper surface of the substrate W move between the central portion and the peripheral edge portion in this state.

The SPM discharged from the first chemical liquid nozzle **11** lands on the upper surface of the substrate W and thereafter flows outward along the upper surface of the substrate W due to a centrifugal force. The SPM is thus supplied to the entirety of the upper surface of the substrate W and a liquid film of SPM that covers the entire upper surface of the substrate W is thereby formed on the substrate W. The resist film and the SPM are thereby made to undergo a chemical reaction and the resist film on the substrate W is removed from the substrate W by the SPM. Further, the controller **3** makes the liquid landing position of the SPM with respect to the upper surface of the substrate W move between the central portion and the peripheral edge portion in the state where the substrate W is rotating so that the liquid landing position of the SPM passes through the entire upper surface of the substrate W and the entire upper surface of the substrate W is scanned. The SPM discharged from the first chemical liquid nozzle **11** is thus supplied to the entire upper surface of the substrate W and the entire upper surface of the substrate W is processed uniformly.

Thereafter, a puddle step of holding the liquid film of SPM on the substrate W in a state where the discharge of SPM is stopped (step S**3** of FIG. **20**) is performed. Specifically, the controller **3** controls the spin motor **10** to decelerate the substrate W to a second chemical liquid rotation speed V**2** (see FIG. **21**), lower than the rotation speed of the substrate W in the first chemical liquid supplying step (first chemical liquid rotation speed V**1**), in the state where the entire upper surface of the substrate W is covered by the liquid film of SPM and makes the substrate W rotate at the second chemical liquid rotation speed V**2**. The centrifugal force applied to the SPM on the substrate W thus weakens and the flow rate of SPM expelled from the substrate W decreases. In the state where the substrate W is rotating at the second chemical liquid rotation speed V**2**, the controller **3** closes the sulfuric acid valve **19** and the first hydrogen peroxide water valve **24** to stop the discharge of SPM from the first chemical liquid nozzle **11**. The liquid film of SPM that covers the entire upper surface of the substrate W is thereby held on the substrate W in the state where the discharge of SPM is stopped. After stopping the discharge of SPM, the controller **3** controls the first nozzle moving device **13** to put the first chemical liquid nozzle **11** on standby above the substrate W.

Also, a heating step (step S**4** of FIG. **20**) of using the infrared heater **58** to heat the substrate W and the SPM on the substrate W at a heating temperature, which is higher than the temperature (first temperature) of the SPM before the SPM is supplied to the substrate W, is performed in parallel to the first chemical liquid supplying step (step S2 of FIG. **20**) and the puddle step (step S3 of FIG. **20**). Specifically, the controller **3** controls the heater moving device **60** to move the infrared heater **58** from the retracted position to the processing position. The infrared heater **58** is thereby positioned above the substrate W. Thereafter, the controller **3** makes the infrared heater **58** start emitting light. The temperature of the infrared heater **58** thus rises to the heating temperature (for example, of not less than 200° C.) that is not less than the boiling point of the SPM at its current concentration and is maintained at the heating temperature.

After the infrared heater **58** starts emitting light at a position above the substrate W, the controller **3** makes the infrared heater **58** move by the heater moving device **60** to make the position of irradiation of the infrared rays with respect to the upper surface of the substrate W move within the upper surface of the substrate W. After the heating of the substrate W by the infrared heater **58** has been performed for a predetermined time, the controller **3** makes the infrared heater **58** stop emitting light in the state where the substrate W is rotating at the second chemical liquid rotation speed V**2** and the liquid film of SPM covering the entire upper surface of the substrate W is held on the substrate W. Thereafter, the controller **3** controls the heater moving device **60** to retract the infrared heater **58** from above the substrate W. The emitting of light and moving of the infrared heater **58** may be performed simultaneously or the moving may be started after the emitting of light.

The controller **3** thus makes the position of irradiation of the infrared rays with respect to the upper surface of the substrate W move within the upper surface of the substrate W in the state where the substrate W is being rotated and therefore the substrate W is heated uniformly. The liquid film of SPM covering the entire upper surface of the substrate W is thus also heated uniformly. The temperature of heating of the substrate W by the infrared heater **58** is set to a temperature not less than the boiling point of the SPM at its current concentration. The SPM on the substrate W is thus heated to the boiling point at its current concentration. In particular, when the temperature of heating of the substrate W by the infrared heater **58** is set to a temperature higher than the boiling point of the SPM at its current concentration, the temperature at the interface of the substrate W and the SPM is maintained at a temperature higher than the boiling point to promote removal of foreign matter (resist film) from the substrate W.

Thereafter, a reaction liquid supplying step (step S**5** of FIG. **20**) of supplying SPM, which is an example of a reaction-liquid-containing liquid to the substrate W, and a reaction liquid concentration changing step (step S**6** of FIG. **20**) of decreasing the proportion of the sulfuric acid mixed with the hydrogen peroxide water to increase the proportion of the hydrogen peroxide water in the SPM discharged toward the substrate W are performed in parallel. Further, in parallel to the reaction liquid supplying step and the reaction liquid concentration changing step, a first temperature decrease suppressing step (step S**7** of FIG. **20**) of supplying pure water, which is an example of a heating fluid having a first intermediate temperature lower than the temperature (first temperature) of the SPM and higher than the temperature (second temperature) of a rinse liquid supplied to the substrate W in a first rinse liquid supplying step (step S**8** of FIG. **20**) to be described below, to the lower surface of the substrate W is performed.

In regard to the reaction liquid supplying step, the controller **3** controls the first nozzle moving device **13** to position the first chemical liquid nozzle **11** at the intermediate position at which the processing liquid discharged from the first chemical liquid nozzle **11** lands on the upper surface intermediate portion of the substrate W. Thereafter, the controller **3** opens the sulfuric acid valve **19** and the hydrogen peroxide water valve **24** to make the SPM (reaction-liquid-containing liquid) of the first temperature be discharged from the first chemical liquid nozzle **11** toward the upper surface of the substrate W that is rotating at the second chemical liquid rotation speed V**2**. The supplying of fresh SPM (reaction-liquid-containing liquid) that has not reacted with the substrate W is thereby started at the upper surface intermediate portion of the substrate W.

After the supplying of the SPM controller **3** controls the first nozzle moving device **13** to move the first chemical liquid nozzle **11** from the upper surface intermediate portion to the upper surface central portion in the state where the substrate W is rotating at the second chemical liquid rotation speed V**2**. The liquid landing position of the SPM with respect to the upper surface of the substrate W is thereby moved to the central portion. Thereafter, the controller **3** closes the sulfuric acid valve **19** and the hydrogen peroxide water valve **24** to stop the discharge of SPM from the first chemical liquid nozzle **11**. In succession, the controller **3** controls the first nozzle moving device **13** to make the first chemical liquid nozzle **11** retract from above the substrate W. The reaction liquid supplying step is thereby ended.

In regard to the reaction liquid concentration changing step, while the reaction liquid supplying step is being performed, the controller **3** adjusts the opening degrees of the sulfuric acid flow control valve **20** and the hydrogen peroxide water flow control valve **25** to change the mixing ratio of sulfuric acid and hydrogen peroxide water while maintaining fixed the discharge flow rate of the reaction-liquid-containing liquid discharged from the first chemical liquid nozzle **11**. As shown in the upper stage in FIG. **21**, the controller **3**, for example, gradually reduces the flow rate of the sulfuric acid supplied to the first chemical liquid nozzle **11** and gradually increases the flow rate of the hydrogen peroxide water supplied to the first chemical liquid nozzle **11**. Eventually, the controller **3** changes the mixing ratio of sulfuric acid and hydrogen peroxide water, for example, from 2 (sulfuric acid) to 1 (hydrogen peroxide water) to 1 (sulfuric acid) to 1 (hydrogen peroxide water) continuously or in steps. The mixing ratio immediately before the discharge of the SPM is stopped is thus set to 1 (sulfuric acid) to 1 (hydrogen peroxide water).

In the reaction liquid concentration changing step, the mixing ratio may be changed gradually after starting processing with the mixing ratio (for example, 10 (sulfuric acid) to 1 (hydrogen peroxide water)) in the first chemical liquid supplying step (step S**2** of FIG. **20**). Further, in the final stage of the reaction liquid concentration changing step, the proportion of the sulfuric acid may be reduced to zero.

In regard to the first temperature decrease suppressing step, the controller **3** makes pure water of the first intermediate temperature (for example, a temperature higher than room temperature) be discharged from the lower surface nozzle **45** toward the lower surface of the substrate W that is rotating at the second chemical liquid rotation speed V**2**. The pure water discharged from the lower surface nozzle **45** lands on the lower surface central portion of the substrate W and thereafter flows outward along the lower surface of the substrate W to the peripheral edge of the substrate W due to a centrifugal force. The pure water is thereby supplied to the entire lower surface of the substrate W. Temperature decrease of the substrate W and the SPM is thus suppressed. After elapse of a predetermined time from the opening of the heating liquid valve **47**, the controller **3** closes the heating liquid valve **47** to stop the discharge of pure water from the lower surface nozzle **45**. Thereafter, the controller **3** opens and closes the gas valve **55** to make nitrogen gas be discharged temporarily from the gas discharge port **53**. The pure water is thereby expelled from between the substrate W and the spin base **7**.

In the reaction liquid supplying step, the proportion of the hydrogen peroxide water contained in the reaction-liquid-containing liquid (SPM) is gradually increased. As the proportion of the hydrogen peroxide water having room temperature increases, the temperature of the reaction-liquid-containing liquid decreases to a temperature lower than the first temperature and not less than room temperature. The reaction-liquid-containing liquid that lands on the upper surface central portion of the substrate W spreads along the substrate W from the liquid landing position to a periphery of the liquid landing position. Further, the reaction-liquid-containing liquid on the substrate W flows outward along the substrate W toward the peripheral edge of the substrate W while flowing along the substrate W in a circumferential direction toward the downstream side of the rotation direction. The reaction-liquid-containing liquid having lower temperature than the substrate W and the SPM is thereby supplied to the entire upper surface of the substrate W covered by the liquid film of SPM. The reaction-liquid-containing liquid thus flows along the substrate W while taking away the heat of the substrate W and the SPM that are higher in temperature than the reaction-liquid-containing liquid.

In the reaction liquid supplying step, the temperatures of the substrate W and the SPM (especially the temperatures at the liquid landing position and the vicinity thereof) decrease because the reaction-liquid-containing liquid, which is lower in temperature than the heating temperature due to the infrared heater **58**, is supplied to the substrate W. However, the sulfuric acid contained in the SPM on the substrate W and the sulfuric acid contained in the reaction-liquid-containing liquid generate heat due to reaction with the hydrogen peroxide water contained in the reaction-liquid-containing liquid and therefore significant decrease of the temperatures of the substrate W and the SPM at the liquid landing position is suppressed or prevented. Further, the temperature decrease amounts of the substrate W and the SPM at the liquid landing position are reduced by the first temperature decrease suppressing step being performed in parallel to the reaction liquid supplying step. Increase of the temperature difference of the substrate W between the liquid landing position and other positions can thus be suppressed. Deformation of the substrate W due to the temperature difference can thus be suppressed and the amount of warping of the substrate W can be reduced.

Further, the reaction liquid concentration changing step is performed in parallel to the reaction liquid supplying step and the amount of reaction heat generated is thus reduced gradually by gradual decrease of the sulfuric acid concentration in the reaction-liquid-containing liquid. The reaction-liquid-containing liquid supplied to the substrate W thus decreases gradually in its temperature. Therefore in the reaction liquid supplying step, the temperatures of the substrate W and the SPM decrease gradually due to the supplying of the reaction-liquid-containing liquid. The temperature difference of the reaction-liquid-containing liquid with respect to the substrate W and the SPM is thus greatest when the supplying of the reaction-liquid-containing liquid is started. The supplying of the reaction-liquid-containing liquid is started at the upper surface intermediate portion of the substrate W at which the circumferential speed is greater than that at the upper surface central portion of the substrate W. Therefore, the supply flow rate of the reaction-liquid-containing liquid per unit area is lower than in a case where the supplying of the reaction-liquid-containing liquid is started at the upper surface central portion of the substrate W. The temperatures of the substrate W and the SPM at the liquid landing position can thus be suppressed or prevented from decreasing suddenly and significantly due to the supplying of a large amount of the reaction-liquid-containing liquid. Further, the reaction-liquid-containing liquid that lands on the upper surface central portion of the substrate W is expelled to the periphery of the substrate W via the upper surface peripheral edge portion of the substrate W and therefore the retention time of the reaction-liquid-containing liquid on the substrate W is longer than in a case where the supplying of the reaction-liquid-containing liquid is started at the upper surface peripheral edge portion of the substrate W. The reaction-liquid-containing liquid can thus be used efficiently.

Also, the first chemical liquid nozzle **11** discharges the reaction-liquid-containing liquid inwardly. Therefore the reaction-liquid-containing liquid discharged from the first chemical liquid nozzle **11** mainly flows inwardly from the liquid landing position along the substrate W. The reaction-liquid-containing liquid can thus be spread to a region further inward than the liquid landing position in a shorter time than in a case where the first chemical liquid nozzle **11** discharges the reaction-liquid-containing liquid in the direction perpendicular to the upper surface of the substrate W or in a case where the first chemical liquid nozzle **11** discharges the reaction-liquid-containing liquid outwardly. Further, the flow rate of the reaction-liquid-containing liquid flowing inwardly from the liquid landing position is increased in comparison to these cases and the retention time of the reaction-liquid-containing liquid on the substrate W is thus increased. The reaction-liquid-containing liquid can thus be used efficiently.

Thereafter, the first rinse liquid supplying step (step S**8** of FIG. **20**) of supplying pure water having room temperature, which is an example of the rinse liquid having the second temperature, to the substrate W is performed. Specifically, the controller **3** controls the third nozzle moving device **38** to move the rinse liquid nozzle **36** from the retracted position to the processing position. Thereafter, the controller **3** opens the first rinse liquid valve **40** to make the pure water having room temperature be discharged from the rinse liquid nozzle **36** toward the upper surface central portion of the substrate W. Further, the controller **3** controls the spin motor **10** to accelerate the substrate W to a rinse rotation speed V**3** greater than the first chemical liquid rotation speed V**1** and the second chemical liquid rotation speed V**2** (see FIG. **21**) and makes the substrate W rotate at the rinse rotation speed V**3**. When a predetermined time has elapsed from the opening of the first rinse liquid valve **40**, the controller **3** closes the first rinse liquid valve **40** to stop the discharge of pure water from the rinse liquid nozzle **36**. Thereafter, the controller **3** controls the third nozzle moving device **38** to make the rinse liquid nozzle **36** retract from above the substrate W.

The pure water discharged from the rinse liquid nozzle **36** lands on the upper surface central portion of the substrate W that is covered by the chemical liquid or the reaction-liquid-containing liquid. The chemical liquid on the substrate W is thus forced to flow away from the central portion to a periphery thereof. The pure water that has landed on the upper surface central portion of the substrate W flows outward along the upper surface of the substrate W due to a centrifugal force. Similarly, the chemical liquid on the substrate W flows outward along the upper surface of the substrate W due to the centrifugal force. Further, the substrate W is rotating at the rinse rotation speed V**3** greater than the first chemical liquid rotation speed V**1** and the second chemical liquid rotation speed V**2** and therefore a greater centrifugal force is applied to the liquid on the substrate W than those applied in the first chemical liquid supplying step and the reaction liquid supplying step. The liquid film of pure water thus spreads instantly from the central portion of the substrate W to the peripheral edge of the substrate W and the chemical liquid on the substrate W is replaced by the pure water in a short time. The chemical liquid on the substrate W is thereby rinsed off by the pure water.

Thereafter, a second chemical liquid supplying step (step S**9** of FIG. **20**) of supplying the SC**1**, which is an example of a second chemical liquid having a temperature before being supplied to the substrate W of less than the temperature (first temperature) of the SPM and higher than the temperature (second temperature) of the rinse liquid, to the substrate W, and a second temperature decrease suppressing step (step S**10** of FIG. **20**) of supplying pure water, which is an example of a heating fluid having a second intermediate temperature, lower than the temperature (first temperature) of the SPM and higher than the temperature (second temperature) of the rinse liquid, as the temperature before being supplied to the substrate W, to the lower surface of the substrate W are performed in parallel.

In regard to the second chemical liquid supplying step, the controller **3** controls the second nozzle moving device **31** to move the second chemical liquid nozzle **29** from the retracted position to the processing position. After the second chemical liquid nozzle **29** has been positioned above the substrate W, the controller **3** opens the second chemical liquid valve **34** to make the SC**1** be discharged from the second chemical liquid nozzle **29** toward the upper surface of the substrate W that is in the rotating state. In this state, the controller **3** controls the second nozzle moving device **31** to make the liquid landing position of the SC**1** with respect to the upper surface of the substrate W move between the central portion and the peripheral edge portion. When a predetermined time elapses from the opening of the second chemical liquid valve **34**, the controller **3** closes the second chemical liquid valve **34** to stop the discharge of the SC**1**. Thereafter, the controller **3** controls the second nozzle moving device **31** to make the second chemical liquid nozzle **29** retract from above the substrate W.

The SC**1** discharged from the second chemical liquid nozzle **29** lands on the upper surface of the substrate W and thereafter flows outward along the upper surface of the substrate W due to the centrifugal force. The pure water on the substrate W is thus forced to flow outward by the SC**1** and is expelled to a periphery of the substrate W. The liquid film of pure water on the substrate W is thereby replaced by the liquid film of SC**1** that covers the entire upper surface of the substrate W. Further, the controller **3** makes the liquid landing position of the SC**1** with respect to the upper surface of the substrate W move between the central portion and the peripheral edge portion in the state where the substrate W is rotating so that the liquid landing position of the SC**1** passes through the entire upper surface of the substrate W and the entire upper surface of the substrate W is scanned. The SC**1** discharged from the second chemical liquid nozzle **29** is thus supplied to the entire upper surface of the substrate W and the entire upper surface of the substrate W is processed uniformly.

In regard to the second temperature decrease suppressing step, the controller **3** makes pure water of the second intermediate temperature be discharged from the lower surface nozzle **45** toward the lower surface of the rotating substrate W. The pure water is thereby supplied to the entire lower surface of the substrate W. The temperature of the substrate W, which has been decreased to the second temperature by the supplying of the rinse liquid having the second temperature, can thereby be prevented from changing locally due to the supplying of the SC**1** having the temperature higher than the second temperature. After elapse of a predetermined time from the opening of the heating liquid valve **47**, the controller **3** closes the heating liquid valve **47** to stop the discharge of pure water from the lower surface nozzle **45**. Thereafter, the controller **3** opens and closes the gas valve **55** to make nitrogen gas be discharged temporarily from the gas discharge port **53**. The pure water is thereby expelled from between the substrate W and the spin base **7**.

Thereafter, a second rinse liquid supplying step (step S**11** of FIG. **20**) of supplying pure water having room temperature, which is an example of the rinse liquid, to the substrate W is performed. Specifically, the controller **3** controls the third nozzle moving device **38** to move the rinse liquid nozzle **36** from the retracted position to the processing position. After the rinse liquid nozzle **36** has been positioned above the substrate W, the controller **3** opens the first rinse liquid valve **40** to make the pure water be discharged from the rinse liquid nozzle **36** toward the upper surface of the substrate W. The SC**1** on the substrate W is thereby forced to flow outward by the pure water and is expelled to the periphery of the substrate W. The liquid film of SC**1** on the substrate W is thus replaced by the liquid film of pure water that covers the entire upper surface of the substrate W. When a predetermined time elapses from the opening of the first rinse liquid valve **40**, the controller **3** closes the first rinse liquid valve **40** to stop the discharge of pure water. Thereafter the controller **3** controls the first nozzle moving device **13** to make the rinse liquid nozzle **36** retract from above the substrate W.

Thereafter a drying step (step S**12** of FIG. **20**) of drying the substrate W is performed. Specifically, the controller **3** controls the spin motor **10** to accelerate the substrate W to a drying rotation speed (for example of several thousand rpm) greater than the rotation speeds in the first chemical liquid supplying step (step S**2** of FIG. **20**) to the second rinse liquid supplying step (step S**11** of FIG. **20**) and makes the substrate W rotate at the drying rotation speed. A large centrifugal force is thereby applied to the liquid on the substrate W and the liquid attached to the substrate W is spun off to the periphery of the substrate W. The substrate W is thereby removed of liquid and the substrate W dries. After a predetermined time elapses from the start of high-speed rotation of the substrate W, the controller **3** controls the spin motor **10** to stop the rotation of the substrate W by the spin chuck **5**.

Thereafter, a carrying-out step (step S**13** of FIG. **20**) of carrying out the substrate W from inside the chamber **4** is performed. Specifically, the controller **3** moves the respective chuck pins **8** from the closed positions to the open positions to release the clamping of the substrate W by the spin chuck **5**. Thereafter in the state where all nozzles, etc., are retracted from above the spin chuck **5**, the controller **3** makes the hand of the substrate transfer robot CR enter inside the chamber **4**. The controller **3** then makes the hand of the transfer robot CR hold the substrate W on the spin chuck **5**. Thereafter, the controller **3** makes the hand of the substrate transfer robot CR retract from inside the chamber **4**. The processed substrate W is thereby carried out of the chamber **4**.

Although a case where a hydrogen-peroxide-water-containing liquid (hydrogen peroxide water or a mixed liquid of sulfuric acid and hydrogen peroxide water) is supplied as the reaction-liquid-containing liquid to the substrate W in the reaction liquid supplying step was described in the above description of the seventh processing example, a pure-water-containing liquid (pure water or a mixed liquid of sulfuric acid and pure water or a mixed liquid of SPM and pure water), containing pure water, which causes an exothermic reaction upon mixing with sulfuric acid, and having a liquid temperature not more than the first temperature and not less than the second temperature, may be supplied instead to the substrate W in the reaction liquid supplying step. Specifically, in place of the reaction liquid supplying step (step S**5** of FIG. **21**) of supplying the hydrogen-peroxide-water-containing liquid to the substrate W, a reaction liquid supplying step (step S**5***a* of FIG. **21**) of supplying the pure-water-containing liquid, which is an example of the reaction-liquid-containing liquid, to the substrate W may be executed in parallel to the reaction liquid concentration changing step and the first temperature decrease suppressing step.

In this case, the controller **3** controls the first nozzle moving device **13** to position the first chemical liquid nozzle **11** at the intermediate position at which the processing liquid discharged from the first chemical liquid nozzle **11** lands on the upper surface intermediate portion of the substrate W. Thereafter, the controller **3** opens the sulfuric acid valve **19** and a pure water valve **427** to make a mixed liquid of sulfuric acid and pure water (pure-water-containing liquid) having a temperature lower than the first temperature and higher than the second temperature be discharged from the first chemical liquid nozzle **11** toward the upper surface of the substrate W that is rotating at the second chemical liquid rotation speed V**2**. The supplying of the mixed liquid of sulfuric acid and pure water (pure-water-containing liquid) is thereby started at the upper surface intermediate portion of the substrate W.

After the supplying of the mixed liquid of sulfuric acid and pure water (pure-water-containing liquid) is started at the upper surface intermediate portion of the substrate W, the controller **3** adjusts the opening degrees of the sulfuric acid flow control valve **20** and a pure water flow control valve **428** to change the mixing ratio of sulfuric acid and pure water while maintaining fixed the discharge flow rate of the pure-water-containing liquid discharged from the first chemical liquid nozzle **11**. As shown in the lower stage in FIG. **21**, the controller **3**, for example, gradually reduces the supply flow rate of the sulfuric acid to gradually decrease the discharge flow rate of the sulfuric acid discharged from the first chemical liquid nozzle **11**. In parallel to this, the controller **3** increases the flow rate of the pure water supplied to the first chemical liquid nozzle **11**. Eventually, the controller **3** reduces the opening degree of the sulfuric acid flow control valve **20** to zero. Therefore eventually, the mixing ratio of sulfuric acid and pure water is changed to 0 (sulfuric acid) to 1 (pure water) and only the pure water (pure-water-containing liquid) having room temperature is discharged from the first chemical liquid nozzle **11**.

Also in parallel to changing the mixing ratio of sulfuric acid and pure water, the controller **3** controls the first nozzle moving device **13** to move the first chemical liquid nozzle **11** from the intermediate position to the central position in the state where the substrate W is rotating at the second chemical liquid rotation speed V**2**. The liquid landing position of the pure-water-containing liquid is thereby moved from the upper surface intermediate portion to the upper surface central portion of the substrate W. Thereafter, the controller **3** starts the first rinse liquid supplying step (step S**8** of FIG. **20**) of supplying the pure water having room temperature, which is an example of the rinse liquid having the second temperature, to the substrate W. Specifically, the controller **3** controls the spin motor **10** to make the substrate W rotate at the rinse rotation speed V**3** in the state where the pure water having room temperature is being discharged from the first chemical liquid nozzle **11** toward the upper surface central portion of the substrate W. Thereafter, the controller **3** closes the pure water valve **427** to stop the discharge of pure water from the first chemical liquid nozzle **11**. In succession, the controller **3** controls the first nozzle moving device **13** to make the first chemical liquid nozzle **11** retract from above the substrate W.

As described above, with the present preferred embodiment, the chemical liquid having the first temperature (the temperature of the chemical liquid before being supplied to the substrate W) is supplied to the upper surface of the substrate W. The reaction-liquid-containing liquid (the liquid containing hydrogen peroxide water or pure water as the reaction liquid) is then supplied to the upper surface of the substrate W in the state where the chemical liquid remains on the substrate W. The reaction-liquid-containing liquid supplied to the substrate W mixes with the chemical liquid remaining on the substrate W. The proportion of the reaction-liquid-containing liquid in the liquid remaining on the substrate W thus increases and the concentration of the chemical liquid decreases. The rinse liquid having the second temperature (the temperature of the rinse liquid before being supplied to the substrate W) lower than the first temperature is supplied to the upper surface of the substrate W after the reaction-liquid-containing liquid has been supplied to the substrate W. The liquid remaining on the substrate W (the liquid containing the chemical liquid and the reaction-liquid-containing liquid) is thereby rinsed off.

When the supplying of the reaction-liquid-containing liquid is started, the temperature of the substrate W approaches the temperature of the reaction-liquid-containing liquid. The temperature of the reaction-liquid-containing liquid before being supplied to the substrate W is not more than the temperature (first temperature) of the chemical liquid and not less than the temperature (second temperature) of the rinse liquid. Upon mixing with the chemical liquid (SPM), the reaction liquid (hydrogen peroxide water or pure water) contained in the reaction-liquid-containing liquid causes an exothermic reaction. Therefore, when the reaction-liquid-containing liquid is supplied to the upper surface of the substrate W in the state where the chemical liquid remains on the substrate W, the exothermic reaction occurs at the liquid landing position of the reaction-liquid-containing liquid and at positions in its vicinity so that the temperature decrease amount of the substrate W is reduced in the liquid landing position vicinity region. The temperature of the substrate W thus approaches the temperature of the reaction-liquid-containing liquid gradually. That is, sudden temperature change of the substrate W is suppressed.

Further, the proportion of the heat generating liquid (sulfuric acid or SPM) contained in the reaction-liquid-containing liquid decreases from that at the start of discharge of the reaction-liquid-containing liquid so that the proportion of the reaction liquid (hydrogen peroxide water or pure water) having lower temperature than the heat generating liquid increases and consequently, the temperature of the reaction-liquid-containing liquid decreases. Therefore, the reaction-liquid-containing liquid having lower temperature than the reaction-liquid-containing liquid at the start of discharge is supplied to the upper surface of the substrate W and the temperature of the reaction-liquid-containing liquid approaches the temperature (second temperature) of the rinse liquid. The temperature decrease of the substrate W in the liquid landing position vicinity region is thus made even more gradual. Sudden and rapid temperature decrease of the substrate W can thus be suppressed to reduce the amount of deformation of the substrate W in comparison to a case where the pure water having room temperature is supplied to the substrate W in succession to the supplying of the SPM having high temperature.

Also with the present preferred embodiment, the reaction-liquid-containing liquid, in which the proportion of the heat generating liquid (SPM) is large, is discharged toward the upper surface of the substrate W. Thereafter, the proportion of the heat generating liquid contained in the reaction-liquid-containing liquid is reduced. The temperature of the reaction-liquid-containing liquid that is discharged toward the substrate W thus decreases greatly gradually. Therefore, even when the temperature difference of the chemical liquid and the rinse liquid is large, that is, even when the difference between the first temperature and the second temperature is large, the temperature of the substrate W can be made to approach the temperature of the rinse liquid gradually and yet uniformly. Deformation of the substrate W due to temperature difference can thereby be suppressed or prevented.

Also with the present preferred embodiment, the proportion of the heat generating liquid (sulfuric acid) contained in the reaction-liquid-containing liquid is reduced to zero. The heat generating liquid contained in the reaction-liquid-containing liquid is thus eliminated and only the reaction liquid (pure water) is discharged toward the substrate W. The temperature of the reaction-liquid-containing liquid that is discharged toward the substrate W thus decreases greatly gradually and the temperature change amount of the reaction-liquid-containing liquid increases. Therefore, even when the temperature difference of the chemical liquid and the rinse liquid is large, the temperature of the substrate W can be made to approach the temperature of the rinse liquid gradually and yet uniformly.

Also with the present preferred embodiment, the reaction-liquid-containing liquid is made up of sulfuric acid and pure water and the proportion of the heat generating liquid (sulfuric acid) contained in the reaction-liquid-containing liquid is reduced to zero. The heat generating liquid contained in the reaction-liquid-containing liquid is thus eliminated and only the reaction liquid, that is, the same type of liquid as the rinse liquid supplied to the substrate W in the second rinse liquid supplying step (step S**8** of FIG. **20**) is discharged toward the substrate W. Therefore not only does the temperature of the reaction-liquid-containing liquid decrease greatly gradually but the affinity of the liquid, remaining on the substrate W before the second rinse liquid supplying step (step S**8** of FIG. **20**), and the rinse liquid is increased as well. The liquid remaining on the substrate W can thus be rinsed off smoothly by supplying the rinse liquid after supplying the reaction-liquid-containing liquid.

Other Preferred Embodiments

Although the preferred embodiments of the present invention have been described above, the present invention is not restricted to the contents of the above-described preferred embodiments and various modifications are possible within the scope of the present invention.

For example, although with each of the processing examples described above, the case where the puddle step of making the substrate W and the SPM react is performed in the state where the discharge of SPM from the first chemical liquid nozzle **11** is stopped was described, the puddle step may be omitted and the reaction liquid supplying step may be started in succession to the end of the first chemical liquid supplying step.

Also, although with each of the processing examples, the case where the substrate W and the SPM are heated by the infrared heater **58** was described, the heating step of heating the substrate W and the SPM by the infrared heater **58** (step S**4** of FIG. **5**) may be omitted.

Also, although with each of the processing examples, the case where the first temperature decrease suppressing step is started at the same time as the reaction liquid supplying step (step S**5** of FIG. **5**) was described, the first temperature decrease suppressing step (step S**6** of FIG. **5**) may be started before the start or after the start of the reaction liquid supplying step. Similarly, the second temperature decrease suppressing step (step S**9** of FIG. **5**) may be started before the start or after the start of the second chemical liquid supplying step (step S**8** of FIG. **5**).

Also, although with each of the processing examples, the case where the second temperature decrease suppressing step (step S**9** of FIG. **5**) is started after the first temperature decrease suppressing step (step S**6** of FIG. **5**) is ended, that is, after the discharge of the heating fluid is stopped was described, the discharge of the heating fluid may be continued from the start of the reaction liquid supplying step (step S**5** of FIG. **5**) to the end of the second chemical liquid supplying step (step S**8** of FIG. **5**).

Also, although with each of the processing examples, the case where the processing unit **2** performs the resist removing process was described, the process performed by the processing unit **2** is not restricted to the resist removing process and may be another process, such as a cleaning process or an etching process, etc.

Also, although with each of the preferred embodiments described above, the case where the spin chuck **5** is a clamping type chuck that includes the plurality of chuck pins **8** was described, the spin chuck **5** may instead be a vacuum type chuck with which the lower surface (rear surface) of the substrate W is suctioned onto an upper surface of a spin base (suction base).

Also, although with each of the preferred embodiments, the case where the first chemical liquid nozzle **11**, the second chemical liquid nozzle **29**, and the rinse liquid nozzle **36** are mounted on separate nozzle arms was described, two or more of the nozzles may be mounted on a nozzle arm in common. Similarly, the infrared heater **58** may be mounted on an arm in common with the first chemical liquid nozzle **11** or other processing liquid nozzle that discharges a processing liquid.

Also, although with each of the preferred embodiments, the case where two pipings (the first hydrogen peroxide water piping **23** and the second hydrogen peroxide water piping **26**) that supply the hydrogen peroxide water to the first chemical liquid nozzle **11** are provided was described, one of these pipings may be omitted. Similarly, although the case where two pipings (the first rinse liquid piping **39** and the second rinse liquid piping **42**) that supply the rinse liquid to the rinse liquid nozzle **36** are provided was described, one of these pipings may be omitted.

Also, although with each of the preferred embodiments, the case where the temperature of the reaction liquid (hydrogen peroxide water or pure water) before being supplied to the substrate is room temperature was described, the temperature of the reaction liquid before being supplied to the substrate may be higher than room temperature as long as it is lower than the temperature (first temperature) of the SPM before being supplied to the substrate.

Also, although with each of the preferred embodiments, the case where warm water (pure water heated to the first intermediate temperature), which is an example of the heating liquid, is supplied to the lower surface of the substrate W was described, a heating gas may be supplied instead of a heating liquid to the lower surface of the substrate W.

Specifically, in at least one of either of the first temperature decrease suppressing step (step S**6** of FIG. **5**) or the second temperature decrease suppressing step (step S**9** of FIG. **5**), the controller **3** may open the gas valve **55** to make nitrogen gas of the first intermediate temperature (for example, a temperature higher than room temperature) be discharged from the gas discharge port **53** that opens at the upper surface central portion of the spin base **7**. In this case, the nitrogen gas discharged from the gas discharge port **53** spreads radially in the space between the lower surface of the substrate W and the upper surface of the spin base **7** from the upper surface central portion of the spin base **7**. The space between the lower surface of the substrate W and the upper surface of the spin base **7** is thereby filled with the nitrogen gas of the first intermediate temperature and the temperature decrease of the substrate W is suppressed by the nitrogen gas, which is an example of the heating gas.

Also, although with the seventh processing example, the case where the substrate W and the SPM are heated by the infrared heater **58** was described, the heating step of heating the substrate W and the SPM by the infrared heater **58** (step S**4** of FIG. **20**) may be omitted. Similarly, at least one of either of the first temperature decrease suppressing step (step S**7** of FIG. **20**) and the second temperature decrease suppressing step (step S**10** of FIG. **20**) may be omitted.

Also, although with the seventh processing example, the case where the supplying of the reaction-liquid-containing liquid to the upper surface of the substrate W is started at the upper surface intermediate portion of the substrate W was described, the supplying of the reaction-liquid-containing liquid may be started at a position besides the upper surface central portion of the substrate W (for example, at the upper surface peripheral edge portion).

Also, although with the seventh processing example, the case where the mixing ratio of sulfuric acid and hydrogen peroxide water is eventually changed to 1 (sulfuric acid) to 1 (hydrogen peroxide water) was described, the proportion of sulfuric acid may eventually be reduced to zero so that only the hydrogen peroxide water (hydrogen-peroxide-water-containing liquid) having room temperature is discharged from the first chemical liquid nozzle **11**.

Also, although with the seventh processing example, the case where the first temperature decrease suppressing step is started at the same time as the reaction liquid supplying step (step S**5** of FIG. **20**) was described, the first temperature decrease suppressing step (step S**7** of FIG. **20**) may be started before the start or after the start of the reaction liquid supplying step. Similarly, the second temperature decrease suppressing step (step S**10** of FIG. **20**) may be started before the start or after the start of the second chemical liquid supplying step (step S**9** of FIG. **20**).

Also, although with the seventh processing example, the case where the second temperature decrease suppressing step (step S**10** of FIG. **20**) is started after the first temperature decrease suppressing step (step S**7** of FIG. **20**) is ended, that is, after the discharge of the heating fluid is stopped was described, the discharge of the heating fluid may be continued from the start of the reaction liquid supplying step (step S**5** of FIG. **20**) to the end of the second chemical liquid supplying step (step S**9** of FIG. **20**).

Also, although with the seventh processing example, the case where the processing unit **2** performs the resist removing process was described, the process performed by the processing unit **2** is not restricted to the resist removing process and may be another process, such as a cleaning process or an etching process, etc.

Also, although with the seventh processing example, the case where the reaction-liquid-containing liquid (mixed liquid of sulfuric acid and hydrogen peroxide water or mixed liquid of sulfuric acid and pure water) that has been mixed in advance is supplied to the first chemical liquid nozzle **11** was described, the reaction-liquid-containing liquid may be mixed on the substrate W instead. For example, in the case where the reaction-liquid-containing liquid is the mixed liquid of sulfuric acid and pure water, the first chemical liquid nozzle **11** may discharge sulfuric acid and the rinse liquid nozzle **36** may discharge pure water at the same time.

Also, although with each of the preferred embodiments described above, the case where the spin chuck **5** is a clamping type chuck that includes the plurality of chuck pins **8** was described, the spin chuck **5** may instead be a vacuum type chuck with which the lower surface (rear surface) of the substrate W is suctioned onto an upper surface of a spin base (suction base).

Also, although with each of the preferred embodiments, the case where the first chemical liquid nozzle **11**, the second chemical liquid nozzle **29**, and the rinse liquid nozzle **36** are mounted on separate nozzle arms was described, two or more of the nozzles may be mounted on a nozzle arm in common. Similarly, the infrared heater **58** may be mounted on an arm in common with the first chemical liquid nozzle **11** or other processing liquid nozzle that discharges a processing liquid.

Also, although with each of the preferred embodiments, the case where warm water (pure water heated to the first intermediate temperature), which is an example of the heating liquid, is supplied to the lower surface of the substrate W was described, a heating gas may be supplied instead of a heating liquid to the lower surface of the substrate W.

Specifically, in at least one of either of the first temperature decrease suppressing step (step S**7** of FIG. **20**) or the second temperature decrease suppressing step (step S**10** of FIG. **20**), the controller **3** may open the gas valve **55** to make nitrogen gas of the first intermediate temperature (for example, a temperature higher than room temperature) be discharged from the gas discharge port **53** that opens at the upper surface central portion of the spin base **7**. In this case, the nitrogen gas discharged from the gas discharge port **53** spreads radially in the space between the lower surface of the substrate W and the upper surface of the spin base **7** from the upper surface central portion of the spin base **7**. The space between the lower surface of the substrate W and the upper surface of the spin base **7** is thereby filled with the nitrogen gas of the first intermediate temperature and the temperature decrease of the substrate W is suppressed by the nitrogen gas, which is an example of the heating gas.

Also, although with each of the preferred embodiments, the case where the substrate processing apparatus **1** is an apparatus that processes the disk-shaped substrates W was described, the substrate processing apparatus **1** may instead be an apparatus that processes polygonal substrates W, such as substrates for liquid crystal displays, etc.

Also, any two or more of the preferred embodiments described above may be combined.

The present application corresponds to Japanese Patent Application No. 2013-181508 and Japanese Patent Application No. 2013-181510 filed on Sep. 2, 2013 in the Japan Patent Office, and the entire disclosures of these applications are incorporated herein by reference.

While preferred embodiments of the present invention have been described in detail above, these are merely specific examples used to clarify the technical contents of the present invention, and the present invention should not be interpreted as being limited only to these specific examples, and the spirit and scope of the present invention shall be limited only by the appended claims.

What is claimed is:

1. A substrate processing method comprising:

a chemical liquid supplying step of supplying a chemical liquid having a first temperature to a major surface of a substrate;

a rinse liquid supplying step of supplying, after the chemical liquid supplying step, a rinse liquid having a second temperature lower than the first temperature to the major surface of the substrate to rinse off the liquid remaining on the substrate;

a reaction liquid supplying step of discharging, after the chemical liquid supplying step and before the rinse liquid supplying step, a reaction-liquid-containing liquid, which contains, at least at a start of discharge of itself, a reaction liquid, causing an exothermic reaction upon mixing with the chemical liquid supplied to the substrate in the chemical liquid supplying step, and a heat generating liquid, generating heat upon mixing with the reaction liquid, and has a liquid temperature not more than the first temperature and not less than the second temperature, toward the major surface of the substrate in a state where the chemical liquid supplied to the substrate in the chemical liquid supplying step remains on the substrate; and

a reaction liquid concentration changing step of reducing, in parallel to the reaction liquid supplying step, a proportion of the heat generating liquid contained in the reaction-liquid-containing liquid discharged toward the substrate such that a liquid temperature of the reaction-liquid-containing liquid discharged toward the substrate decreases to a temperature lower than a liquid temperature of the reaction-liquid-containing liquid at the start of discharge of the reaction-liquid-containing liquid.

2. The substrate processing method according to claim **1**, wherein the reaction liquid concentration changing step includes a step of changing a mixing ratio of the reaction liquid and the heat generating liquid from a first mixing ratio, in which the proportion of the heat generating liquid is greater than the proportion of the reaction liquid, to a second mixing ratio, in which the proportion of the heat generating liquid is less than the proportion of the reaction liquid, to reduce the proportion of the heat generating liquid contained in the reaction-liquid-containing liquid discharged toward the substrate and decrease the temperature of the reaction-liquid-containing liquid discharged toward the substrate to lower than the temperature of the reaction-liquid-containing liquid at the start of discharge of itself.

3. The substrate processing method according to claim **1**, wherein the reaction liquid concentration changing step includes a step of reducing the proportion of the heat generating liquid contained in the reaction-liquid-containing liquid discharged toward the substrate to zero to decrease the temperature of the reaction-liquid-containing liquid discharged toward the substrate to lower than a temperature of the reaction-liquid-containing liquid at the start of discharge of itself.

4. The substrate processing method according to claim **1**, wherein the chemical liquid supplied to the substrate in the chemical liquid supplying step is a mixed liquid of a reaction chemical liquid and a heat generating chemical liquid that is higher in temperature than the reaction chemical liquid and generates heat upon mixing with the reaction chemical liquid, and

the reaction-liquid-containing liquid at the start of discharge of itself is a mixed liquid of the reaction chemical liquid as the reaction liquid and the heat generating chemical liquid as the heat generating liquid.

5. The substrate processing method according to claim **1**, wherein the chemical liquid supplied to the substrate in the chemical liquid supplying step is a mixed liquid of a reaction chemical liquid and a heat generating chemical liquid that is higher in temperature than the reaction chemical liquid and generates heat upon mixing with the reaction chemical liquid, and

the reaction-liquid-containing liquid at the start of discharge of itself is a mixed liquid of the reaction liquid that causes the exothermic reaction upon mixing with the chemical liquid supplied to the substrate in the chemical liquid supplying step and a heat-generating-chemical-liquid-containing liquid containing the heat generating chemical liquid and serving as the heat generating liquid.

6. The substrate processing method according to claim **1**, wherein the reaction liquid is a liquid that is the same in composition as the rinse liquid supplied to the substrate in the rinse liquid supplying step and causes the exothermic reaction upon mixing with the chemical liquid supplied to the substrate in the chemical liquid supplying step, and

the reaction liquid concentration changing step includes a step of reducing the proportion of the heat generating liquid contained in the reaction-liquid-containing liquid discharged toward the substrate to zero to decrease the temperature of the reaction-liquid-containing liquid discharged toward the substrate to lower than the temperature of the reaction-liquid-containing liquid at the start of discharge of itself and make a composition of the reaction-liquid-containing liquid discharged toward the substrate match a composition of the rinse liquid supplied to the substrate in the rinse liquid supplying step.

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